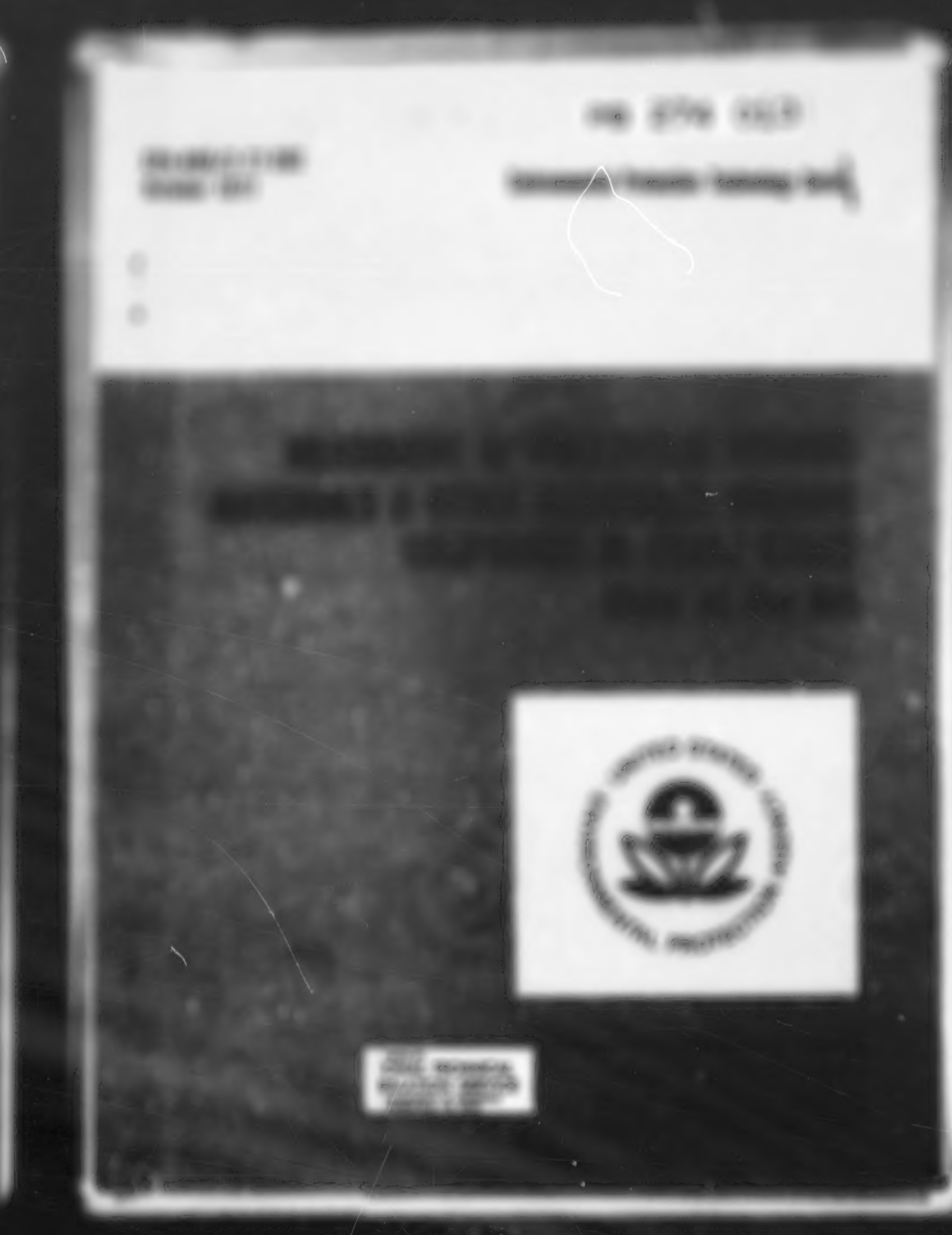

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ABSTRACT

This report documents and reviews state-of-the-art methods for the measurement of principle organic species (POS) and other hazardous organic materials which are present in industrial stack emissions. Emissions sampling for more hazardous compounds, such as PCB and dioxin/furans, are presented and, where specific methods have not been previously reported, the existing sampling with recommended methods provides useful guidance. Individual chapters are devoted to analytical methodology and discussions source sampling methodology, although an effective measurement strategy demands input from both processes. An attempt is made to present a unified approach to hazardous organic emission measurements so that future studies may benefit through more consistent interpretations and more precise and accurate measurements.

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SECTION 1

INTRODUCTION

Together with the long overdue increase in awareness of environmental contamination, an urgent need has arisen for reliable methods for the measurement of pollutant species. This report is concerned with the state-of-the-art methods for measurement of hazardous organic compounds in stack gases. Although the chemical analysis methodologies described here are applicable to organic materials from any source, the sampling methods and sample preparation descriptions pertain to stack gas emissions.

The goal of this report is to present a discriminating review of recent measurement methods for hazardous organic compounds. While not pretending to be an exhaustive bibliography, it attempts to provide an effective source of reference for future measurement problems. Measurement methods for many hazardous compounds, including POMs and nitrosamines, for example, are presented in detail. However, where specific methods have not been previously reported, the sections dealing with generally recommended methods will frequently provide useful guidance.

The rationale for a report which reviews and recommends methods for the measurement of hazardous materials which may potentially enter the environment, is the singular lack of agreement over which experimental methods are appropriate. Thus, this document is an attempt to provide a more unified approach to the measurement of hazardous organic pollutants, with the result that future studies may benefit through providing more realistic intercomparison, and more precise absolute measurements. The two chapters which follow are separately devoted to analytical methodology and sampling methodology, although an effective measurement strategy demands input from each protocol.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In the measurement of organic materials present in stack gases, it is evident that the three distinct areas of importance are sampling, sample preperation, and analysis. The degree of confidence in each area varies depending upon the species sought, but in general there is most confidence in analysis, and probably least in sample preparation or sampling.

Significant recent analytical advances have been made through the use of high performance liquid chromatography and capillary columns in gas chromatographic separations; further development of these important separation techniques and the efficient interface of the former with mass spectrometry would be very desirable. The further development of the interface between gas chromatography and infrared spectroscopy, and an examination of the utility of negative ion mass spectrometry for the analysis of electron capturing species such as PCBs, should be undertaken.

While current extraction and sample recovery procedures generally show good efficiency, further research into sample recovery from dilute solutions is required, in view of losses of more volatile species.

Present stack sampling methods involving cyclones, filters, and polymeric adsorbents are a very significant improvement over earlier methods, but are relatively untried in field sampling situations. It would be highly desirable for field sampling studies to be carried out in order to provide complete validation of these methods under real-world conditions.

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[illegible] gas chromatography and high-performance liquid chromatography, [illegible] used to study drug [illegible] chemistry [illegible] as Research 5). High [illegible] chromatography (HPLC) has been used to monitor the progress of the [illegible] and provide preliminary analysis of the chemical [illegible] of separation and [illegible] using as [illegible] 5 ml glass capillary column and [illegible] a loop as part of the separation scheme for PAH compounds [illegible] to date. Extensive analysis has not attempted in this instance.

Liquid chromatography (LC) and thin layer chromatography (TLC) have been used extensively in PAH separations. Sawicki (12) and Sawicki (13) described methods of forming PAHs to TLC on alumina plates with fluorescence detection, while five aromatic aldehydes and acetylated derivatives, [illegible] coupled to fluorescence detection, is described by Pierce and Taha (14). However, in the matrix of complex environmental mixtures, such techniques do generally inadequate facilitate measurement of large numbers of individual species. Nevertheless, LC is frequently utilized as a preliminary cleanup step prior to GC figure of PAHs, although there is no doubt that a more efficient technique in this manner can be accomplished by high performance liquid chromatography (HPLC). Such [illegible] has been carried out using [illegible] impregnated GF glass gel eluted with 1 percent acetonitrile in [illegible] to separate PAHs from aromatics (15). Sawicki (16,17, 11) has described [illegible] cleanup procedure involving separation of PAHs on activated alumina. HPLC has been used to several workers for the measurement of [illegible] samples for PAHs, and although [illegible] resolution is presently lower as [illegible] to GC, the major drawback of HPLC measurement techniques to its incompatibility with sufficiently sensitive and selective detectors. Recent mass spectrometer interfaces introduced by Finnigan apparently suffer from very poor efficiency (5 percent or less) which precludes satisfactory [illegible] analysis of PAHs.

Most reported LC measurements of PAHs have made use of either ultraviolet (UV) or refractive index (RI) detection, although greater sensitivity and selectivity can be achieved by fluorescence detection if there are no [illegible] quenching [illegible]. Bimbach (11,13,14) describes HPLC analysis schemes which achieve separation of the homologous [illegible] of HPLC-Bath polymers to a [illegible] on 10 column with various polar solvents, to obtain gas separations (11). Detection limits with a 4:1 percent acetylated column of carbon paper, around 200 ng BaP (13). [illegible] cellulose acetate has been found to be a better column packing since it is granular and possesses [illegible] linear cooling capacity than regular cellulose acetate. The structure is more uniform and thus has a greater permeability with lower pressure than the also described system. This separation was achieved on a 250 x 5 mm stainless-steel column of 35 percent HPLC-Bath, Cab-O-Si-308 with a solvent system of 2% ethanol-dichloromethane at a pressure of 3 atm, with a flow rate of 42 ml/h. The UV detection limit measured at 297 nm was 30 ng BaP/3 µl injection & the use of a fluorescence detector with a 320-380 nm excitation filter and a 377 nm emission filter. Since interfering anthracenes often exists in complex PCB mixtures, it was necessary to cleanup the sample on an aluminum oxide/LC column prior to the HPLC procedure.

Boden (23) compared three HPLC column-solvent systems using a UV detector set at 383 nm for quantitation of BaP and at 275 nm for less selective measure-

[illegible]. The three systems are:

(a) 30 cm x 3.2 mm borosilicate column slurry packed with [illegible] at a flow rate of 0.2-0.4 ml/min. The detection limit was 0.1 ng.

(b) 30 cm [illegible] stainless steel WCOT [illegible]: [illegible] at a flow rate of 1.5-4 ml/min. The detection limit was 1 ng.

(c) 30 cm Pyrex WCOT coated with [illegible] at 1-4 ml/min. The detection limit was 1 ng.

While column (a) was the most sensitive, column (c) achieved the best separation of DDT from interfering compounds.

A routine analysis for PCB using HPLC has been described by Jung et al (26). After extracting particulate containing filters in cyclohexane, the sample was preconcentrated on silica gel TLC plates using cyclohexane-benzene (1.5:1.0) as the mobile phase. Separation by HPLC was subsequently achieved on a 25 cm x 2.1 mm ODS Zorbax column using [illegible] (85:15) as the eluting solvent. A fixed wavelength (254 nm) UV detector was used for quantification and identification, the method is sensitive for sub-microgram quantities, with a detection limit of 10 ng DDT routinely achieved.

Ogawa et al (27) have described a sensitive HPLC method using a fluorimetric detector for the analysis of PCBs. Separation was carried out on a Zorbax ODS packed column using a (30:70) water and methanol eluent. The detector was a spectrofluorimeter equipped with a 3 µl volume flow cell, wavelengths being optimised for specific PCBs. At an excitation wavelength of 280 nm and an emission wavelength of 430 nm, a detection limit of 1 ng for DDT was achieved.

A further technique with limited usefulness to the measurement of PCBs is low resolution mass spectrometry using low ionisation potential. Brown et al (28) have used this technique to measure PCBs in the aromatic fraction of samples separated on an alumina column. Quantitation was based on the intensities observed for parent ion peaks. Triphenylbenzene was used as an internal standard for quantification. The ionising voltage of the MS was 11 volts and the sample was scanned from m/e 150 to m/e 400. Low voltage mass spectrometry was also used for quantitation of PCB in oil and emission samples by Thornley et al (29). A major drawback of this technique is that it is not possible to differentiate between isomers; nevertheless, it is an effective screening technique for PCB compounds.

POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED NAPHTHALENES

PCBs and PCNs are found as complex mixtures of substituted biphenyls and naphthalenes, respectively, with various numbers of chlorine atoms. Theoretically, there are 210 possible PCB isomers, although in practice much smaller numbers of each of these classes of compounds are observed.

PCBs and PCNs are most commonly analysed by means of gas chromatography using electron capture detection. While the use of capillary columns significantly improves the isomer resolution which may be achieved, the use of mass spectrometric detection permits more definative structure assignments to be made.

Bowes reported GC separations of PCBs and PCBs within a combination of OV-1 with either of OV-7, OV-17, OV-101, or SE-30, as the stationary phase. Fishbein (26) has reviewed numerous chromatographic techniques for PCBs and describes the use of a tritium electron capture detector in conjunction with a 6 ft x 1/8 in OD glass column packed with 6 percent OV-1 and 4 percent SE-30 on acid washed Chromosorb W. The operating conditions were: column temperature 200 C, nitrogen carrier gas, injector temperature 250 c, and the detector base temperature 250 C. Mussy et al (30) have described the analysis of PCBs on a 1.5 ft x 4 mm glass column packed with 1.5 percent OV-17 and 1.95 percent OV-1 on Gas Chrom Q (100-120 mesh) at 200 C using argon carrier gas; the 63 Ni electron capture detector was maintained at a temperature of 300 C. Creaihow et al (31) achieved PCB separations using a column packing of 15 percent OV-1 and 10 percent DC-200 silicone (1:1) on 60/100 mesh Chromosorb W, in addition to a 3 percent OV-1 on 60/80 mesh Gas Chrom Q which was utilized in a GC-MS application.

Krupcik et al (32) have investigated the application of capillary gas chromatography to the analysis of PCBs, and found that metal capillary columns coated with Apiezon L or OV-101 were inferior to 30 or 60 m glass capillary columns coated with OV-101. Preferred chromatographic conditions were: column temperature 200 C; injection port temperature 250 C; nitrogen flow rate 0.3-0.7 ml/min. These workers additionally reported the use of capillary column GC-MS analysis of PCBs using a 30 m glass capillary column coated with SE-30 at 200 C. Both the injection port and the ion source temperature were maintained at 250 C; the helium flow rate was 0.5 ml/min. Mass spectra, used for the identification of isomeric PCBs, were obtained from nanogram quantities of the unknowns. Dierens and Veit (33) have utilized a 50 ft Scot Apiezon L column for the measurement of PCBs in commercial mixtures, but achieved somewhat lower resolution than the previous workers.

Quantitation of PCBs obtained by perchlorinating to decachlorobiphenyl or by dechlorination to bicyclohexyl and subsequently detecting these derivatives by gas chromatographic methods has been described by Berg et al (34). However, it should be cautioned that unpublished reports have indicated that perchlorination with antimony pentachloride is susceptible to interference from decachlorobiphenyl which appears to be generated during the reaction (35), from sources other than the PCB content of the sample.

PCBs may be catalytically dechlorinated over Pt or Pd catalysts and "total PCB" subsequently quantified by measurement of biphenyl using GC, as described earlier. However, since this dechlorination is not always quantitative, and in the absence of mass spectrometric detection, catalytic perchlorination is preferred in view of the greater sensitivity of electron capture detectors towards the perchlorination product. Perchlorination of PCBs has been carried out by Berg et al (34), using antimony pentachloride, the resultant solution was then treated with 20 percent HCl to prevent the precipitation of oxychloride. The aqueous phase was extracted with warm benzene, shaken with aqueous bicarbonate, and finally with water. The organic layer was dried over anhydrous sodium sulfate. Decachlorobiphenyl was detected by a tritium detector at 215 C after chromatography on a 5 percent SE-30 column at 215 C, with an injector temperature of 220 C.

Armour (38) found that, for PCBs of low chlorine content, Berg's method was not reproducible, and attributed this to volatilization during evaporation of the solvent from the sample. It was recommended that the PCB sample should be perchlorinated in a 0.1 ml solution of chloroform and the derivative chromatographed on either a 1 percent OV-101 or a 3 percent Dexsil column using an EC detector.

The main drawback of the perchlorination measurement method is that biphenyl must be completely removed from the sample prior to perchlorination to avoid erroneously high levels of decachlorobiphenyl. Brinkman et al describe a high liquid chromatographic (HPLC) technique for the analysis of PCBs. Separation was carried out on a 25 cm x 3 mm silica gel column using n-hexane as the mobile phase. The detector used was a thermostated UV cell with a volume of 8 mm^3 and a 1 cm path-length, detection being carried out at 205 nm it is recommended that a similar procedure should be used to remove biphenyl from PCBs prior to quantitative analysis by perchlorination techniques.

When PCBs and PCNs are to be measured by means of GC with electron capture detection, it is advisable to carry out a preliminary chromatographic cleanup step for the removal of commonly occurring pesticides which would otherwise interfere with subsequent analysis. Column chromatography on Florisil (37,38 is often used for cleanup of samples, however, this is not effective for separating PCBs from all other chlorinated pesticides. Armour and Burke (39) used a column of silicic acid-Celite to elute PCBs with petroleum ether to elution of pesticides (such as DDT and its analogs). The mobile phase was a mixture of acetonitrile, hexane and methylene chloride. Berg et al (34) found that the reproducibility of this method was poor and thus developed a technique involving a column of Fischer coconut charcoal. PCBs were eluted with benzen followed by a Florisil cleanup prior to quantitation by EC gas chromatography. The separation of PCBs from DDT has also been accomplished by means of absorption liquid chromatography on a Merkosorb SI-60 column, using light petroleum solvent (38), and by using Perisorb A with n-hexane as the mobile phase (40).

NITROSAMINES

The majority of nitrosamine analyses which have been reported have concerned measurements on food products. Very few examples of nitrosamine analyses on ambient atmospheres have been described (41,42), and none have specifically concerned the measurement of nitrosamines in stack gas effluents. The following review of analytical methodology describes a variety of techniques which may be generally applied to stack gas effluent.

A considerable proportion of reported nitrosamine measurements involve derivatization, oxidation, or reduction of the nitrosamine, followed by gas chromatographic analysis utilizing electron capture detection. Remarkably good sensitivities have been achieved by these techniques, frequently as low as 10-100 pg, but despite the use of relatively selective electron capture detectors, structure confirmation is nevertheless lacking from these techniques. The increased resolution of capillary GC columns is an aid to both qualitative analysis and sensitivity, as discussed subsequently. Furthermore, the use of mass spectrometric detection may facilitate qualitative analysis.

A serious problem which is associated with the measurement of volatile compounds such as nitrosamines, is the maintenance of sample integrity during extraction, concentration, and chromatography. A study by Jones et al (43) demonstrated that typical recoveries for N-nitrosodiethylamine were 65 to 85 percent during sample handling. Castegnaro (44) has described a technique for derivatizing volatile nitrosamines to oxonium salts, in order to avoid sample losses. Nitrosamines were reacted with triethyloxonium fluoroborate in dichloroethane, and after volume reduction, the oxonium salt was oxidized to nitramine prior to subsequent analysis by GC with electron capture detection. Recoveries of approximately 90 percent have been achieved by this technique.

Alliston et al (45) have reported the reduction of nitrosamines electrochemically to secondary amines which were subsequently derivatized to polyfluorinated amides utilizing heptafluorobutanoyl chloride. These derivatives were chromatographed on a 2.75 m x 2 mm 15 percent column of FFAP at 60 C and detected by a ^{63}Ni electron capture detector operated at a pulse space of 500 ns and at a temperature of 250 C. The lower limit of detection was approximately 100 pg.

Eisenbrand (46) utilized acid catalyzed denitrosation and derivatization with heptafluorobutylchloride to form electron capturing derivatives of volatile nitrosamines. Separation was obtained on 5 percent SE-30 column, with a detection limit of 100-200 pg using a ^{63}Ni electron capture detector.

Nitrosamines have been oxidized to nitramines with peroxytrifluoroacetic acid as described by Sen (47). Chromatographic separation of these derivatives was accomplished using a 6 ft, 10 percent Carbowax 20 m column maintained at 150 C, with a tritium electron capture detector at 210 C; a detection limit of approximately 10 pg was achieved with this system.

The thermionic (alkali flame ionization) detector equipped with various salt tips has been found to be selective for nitrogen containing compounds. The rubidium chloride thermionic detector has been shown to have a detection limit of 0.3-0.5 ng by Gough and Sugden (48). Samples were chromatographed on 15 percent FFAP column (5.1 m x 2 mm) at 160 C. The injection port temperature was 160 C and the detector temperature 250 C. However, this detector was found to be less stable and sensitive than the conventional flame ionization detector.

Howard et al (49) analyzed nitrosamines, in amounts as low as 0.1 ng by the use of a coiled potassium chloride thermionic detector following separation on a 3 m x 4 mm 10 percent Carbowax 1500 + 3 percent KOH column maintained isothermally at 80 C for 3 minutes and then programmed to 120 C at 10 C/min. Linearity of the detector response was achieved up to 50 ng with a lower limit of detection of 0.1 ng. Havabata (50) reports that the lifetime of a potassium bromide thermionic detector can be extended by the use of a crystal detector system as opposed to the coil type detector reported by Howard (49). The detection limits are similar for both systems.

Rhoades and Johnson (51) have described the conversion of a Coulson liquid conductivity detector into a specific nitrosamine detector by using argon carrier gas and removing the hydrogenation catalyst from the quartz tube.

The furnace was operated in the range of 400-600 C to pyrolyse the nitrosamine, and ammonia was detected as the thermal degradation product. Chromatography was achieved in this instance on a 10 percent Carbowax 1500 column temperature programmed from 70-150 C at 5 C/min. Sensitivities down to 1 nanogram were achieved by this system. Essigmon (52) has also described use of a Coulson detector for nitrosamines, at sensitivities down to about 10 ng. In this work a 20 percent Carbowax 20 M precolumn was utilized in order to permit large injections to be made, with facilities for venting the solvent peak.

Fine et al (53) have described a thermal energy analyser which can be used as a selective and sensitive detector for n-nitroso compounds including both volatile and non-volatile nitrosamines. The sample (in a solution of dichloromethane) is injected into a flash vaporizer and swept into a heated catalytic pyrolysis chamber by the argon carrier gas. The nitric oxide produced is reacted with ozone to give excited NO_2^* which decays with emission of near infrared light, whose intensity is proportional to the original nitrosamine concentration. Dimethylnitrosamine obtained from air samples was chromatographed at 180 C on a Chromosorb 103 column, and could be detected at a level of 1 ppb. (41) Utilizing a column of 15 percent FFAP on Chromosorb W (6.5 m x 2 mm) at 200 C, analysis of volatile N-nitrosamines at concentrations down to 10 µg/l (0.01 ppt) in samples of drinking water was achieved. (54) The application of this detector system to high performance liquid chromatography has subsequently been described (41).

The analysis of N-nitrosodiethylamine by methane chemical ionization GC-MS has been described by Jones et al (43). Quantification was carried out by specific ion current integration for the molecular ion using pyridine as the internal standard. The detection limit achieved was only 1 to 10 ng in this instance, although a one to two order of magnitude improvement should be attainable by specific ion monitoring (SIM). Gas chromatographic separation was achieved in this instance using a 6 ft 3 percent Silar 10 CP column, which is preferable to Carbowax for GC-MS work on account of the low column bleed.

Capillary GC separations of nitrosamines have been described by Pellizari (42) and Jeyns and Roper (55). The former study used a 100 m glass OV-101 SCOT column, while the latter described the use of a PDEGS 26 m glass capillary column. Both systems used mass spectrometric detection, the greatest resolution and sensitivity being achieved by Pellizari, but no detection limits were given.

Gough and Webb (56,57) have described a high resolution GC-MS analytical system with a sensitivity of approximately 1 ng. Other high resolution mass spectrometric analyses of nitrosamines have been described by Crathorne (58), Telling (59), and Bryce (60).

The use of HPLC in the analysis of nitrosamines has been described by Cox (61). One method is to detect an amine derivative of the reduced nitrosamine following separation using either a 1 m x 2 mm column of Durapac Carbowax 400-Corasel or a 50 cm x 2 mm Carbowax-silica gel Si-60 column. In both cases the mobile phase was 25 percent dioxan-2,2,2,4-trimethylpentane with a flow rate of 0.52 cm/sec and a 26 cm/sec respectively. A second method is a

direct N-nitrosamine detection method using a 1 m x 2 mm column of di(2-cyanoethyl) ether as the mobile phase. The flow rate was 0.6 ml/min. The direct analysis was more sensitive but more prone to interferences than the reduction method. Detection limits were between 1 and 10 µg/kg using variable wavelength UV detection.

Klimisch et al (62) have derivatized nitrosamines by denitrosation and reaction with 7-Cl-4-nitrobenzo-2-oxa-1,3-diazol (NBD-Cl) to form fluorescent compounds. Separation of the NBD derivatives was by HPLC on a 250 x 21 mm silica gel column. The solvent system was cyclohexane:acetic acid ethyl ester: isopropanol (50:50:0.5) with a flow rate of 16.5 ml/hr. The UV (473 nm) detection limit was 25 ng/1.5 µl. This was lowered to 0.5 ng/5 µl by use of a fluorescence detector with an excitation wavelength of 365 nm, and detection at 451 nm.

Separation of nitrosamines can also be achieved by liquid chromatography on Sephadex LH-20 with detection by UV analysis at 230-235 nm. (63) A TLC cleanup procedure is described by Eisenbrand (64). Walters et al (65) describe a polarographic and a UV irradiation technique. Reasonable nitrosamine specificity is obtained by a sensitive plasma chromatographic technique with a detection limit of 10 pg which has been described by Karasek and Denney (66).

OTHER HAZARDOUS ORGANIC COMPOUNDS

Vinyl Chloride

Vinyl chloride monomer is a widely used industrial chemical, which has been recently connected with a rare liver cancer. Most published analytical schemes involve collection of ambient air samples on activated charcoal, followed by thermal or solvent desorption with carbon disulfide prior to GC analysis. The majority of GC separations have been carried out using Chromosorb 102. Detection is most typically by flame ionization detector; the highest reported sensitivities for both this technique and GC-MS being 0.1 ng.

Purcell (67) has separated vinyl chloride on an 18 in x 1/8 in column of Chromosorb 102 (80/100 mesh), and recommends thermal desorption from charcoal at 260 C for recovery of vinyl chloride due to the toxicity of carbon disulfide. The GC column was maintained at ambient temperature during sample desorption, vinyl chloride was eluted at 70 C within 4 minutes. Eluting peaks were detected by flame ionization.

Vinyl chloride samples obtained from stationary stack sources have been analyzed by gas chromatography on a Chromosorb 102 column held isothermally at 155 C. (68) A detection limit of 0.1 to 0.4 ng has been reported by flame ionization detection. Analysis of samples containing down to 6 ppb vinyl chloride was achieved by Ives (69) using a 6 ft x 4 mm column of Poropak Q at 120 C, following thermal desorbtion from Tenax GC. A similar analytical scheme has been reported by Ahlstrom (70), who made use of activated charcoal for sample collection. Other separations of vinyl chloride on Carbowax 20M (71) and Chromosorb 101 (72) have been reported by Ravey and Meyers, respectively. However, it should be remembered that all analyses involving a single GC column and a non-selective detector must be confirmed by a supplementary analytical technique.

Two GC columns have been used by Going (73) for separation and confirmation of the presence of vinyl chloride monomer in ambient air. Analysis was accomplished using a flame ionization detector after separation on a 6 ft x 1/8 in 10 percent column of DC 200 Supelcoport at 150 C (injector and detector 210 C). Confirmation of these results was obtained by chromatography on 6 ft x 1/8 in column of 0.4 percent Carbowax 1500 on Carbopak A at ambient temperature. The injector was 180 C and the detector 210 C. Recovery of vinyl chloride was 90 percent with a detection limit of 10 ppb in ambient air.

Lao (74) et al utilized a GC-MS system in order to perform qualitative and quantitative analyses for vinyl chloride monomer. Chromatographic separation was achieved using a 6 ft x 1/8 in column packed with Chromosorb 102 held isothermally at 145 C; the injector, detector and mass spectrometer source were at a temperature of 250 C. The reported detection limit was 0.1 ng.

The use of a Hall detector has been described by Ernest and Van Lierop (75). The Hall detector is a microelectrolytic conductivity detector which determines the amount of HCl formed by reducing the chromatographed sample with hydrogen in a 15 cm x 2 mm ID quartz tube. Preliminary GC separation was accomplished isothermally at 90 C on a 4 m x 1/8 in stainless steel column of 5 percent SE-30 on Chromosorb G. Detection limits were in low nanogram region.

Baumgardner et al (76) have developed a specific chemiluminescence detector for the GC analysis of vinyl chloride monomer. Chromatographic separation was achieved on a 10 ft x 3/16 in Teflon tube packed with 0.4 percent Carbowax 1500 on Carbopak A at ambient temperature. N_2 is used as carrier gas at 30 cc/min. The detector measures the chemiluminescence produced by the reaction between vinyl chloride and ozone. The wavelength range monitored was 4000-4500 Å, the minimum detectable quantity was 60 ppb in air.

Cedergreen et al (77) have quantified the amount of vinyl chloride present in a sample by a coulimetric method, which is based on the determination of chloride content via coulimetric titration in aqueous of acetic acid. The sample is combusted in O_2 and the HCl formed is subsequently titrated with silver ions. The detection limit reported was rather poor at approximately 1 ppm vinyl chloride.

Freund and Sweger (78) have described a specific analytical procedure based on Stark modulated absorption of IR laser radiation. By superimposing a static electric field of appropriate magnitude and sign, on an electric field sweep and a modulating field, it is possible to Stark shift several vinyl chloride IR transitions into exact coincidence with the laser and subsequently to use phase sensitive detection to observe the absorption signal. This signal is directly proportional to the concentration of the sample, but no detection limit was reported.

Bischloromethyl Ether

Parkes et al (79) have described a gas chromatographic method for the analysis of organics including vinyl chloride and bischloromethyl ether (BCME). BCME was initially trapped on Chromosorb 101 and thermally desorbed at 220 C

onto a GC column packed with Chromosorb 101. The column was programmed to 200 C at 50 C after the sample had been desorbed. The flame ionization detector was at a temperature of 250 C. Helium at a flow rate of 40 ml/min was the carrier gas. Detection was at the ppb level.

Solomon and Kallos (80) have described the formation of electron capturing derivatives of BCME and chloromethylmethyl ether by reaction with the sodium salt of 2,4,6-trichlorophenate. Chromatography was accomplished isothermally at 140 C using a 6 ft x 1/4 in glass column packed with 100/200 mesh glass beads coated with 0.1 percent QF-1 and 6 percent OV-17. The temperature of the sample injector (on-column) and the detector were 175 and 250 C, respectively.

Collier (81) measured BCME at the ppb level by high resolution mass spectroscopy. The intensity of ions at m/e 78·9950 ($ClCH_2$-O-CH_2^+) was measured at a resolution of 3500. Shadoff et al (82) and Evans et al (83) have both objected to this procedure because of the possibility of interferences from other species which may yield the ion monitored, specifically from chloromethylmethyl ether. Evans has also pointed out the possibility of adsorption, regeneration and possible decomposition of BCME in the mass spectrometer. Shadoff has analyzed for BCME by SIM GC-MS using the m/e 79 and 81 ions simultaneously. Identification was dependent on the simultaneous response of m/e 79 and m/e 81 in a 3:1 ratio at the correct retention time on a 4 ft column of Chromosorb 101 at 130 C. Detection was achieved down to a level of 10 ng/µl. Evans obtained greater specificity by monitoring m/e 78·9950 by high resolution mass spectrometry after gas chromatographic separation on a column of 30 percent PEG adipate at 150 C, using resolution of 3800. The lower limit of detection was 0.01 ppb with a 10 l air sample.

Hydrazines

Hydrazines have been measured by various techniques such as titrations, GC and TLC. Dee and Webb (84) have described a GC system that reduces the commonly encountered problems of adsorption and peak tailing. They employed a 1 m column of 10 percent 2-hydrazinopyridine (HyPy) on Fluoropak support isothermally maintained at 80 C, however, this column packing is quite unstable. Santacesaria and Guiffie (85) have described a GC column packing which is much more stable than HyPy but still avoids the complications of peak asymmetry and adsorption. This optimum column packing is a 12 percent mixture of triethanolamine and tetraethylenpentamine (2:5) on a support of 30-60 mesh Chromosorb W, which has been shown to be effective for separation of hydrazine and water.

Flala and Weisburger (86) have described a TLC system which is as sensitive as the GC method of Dee and Webb, and which can resolve the dihydrochloride salts of hydrazine, methylhydrazine, 1,1-dimethylhydrazine and 1,2-dimethylhydrazine. It uses precoated (Avicel cellulose 25 µm thick) glass plates developed with 2-propanol-water-conc. HCl (130:40:30). Folen-Ciocateau reagent was sprayed on the plates and after 20 min they were exposed to NH_3 fumes to develop the blue spots of hydrazines. The limit of detectability was 0.12 µg/cm^2.

Epoxides

Epoxide derivatives of polycyclic aromatic hydrocarbons are thought to be either precursors for carcinogens or carcinogenic in themselves. Morreal et al (88) have separated dimethylbenz(a)anthracene epoxides from the corresponding phenols and diols by column chromatography on 5 percent deactivated alumina eluted with 3 percent dioxane in hexane. They were then derivatized to their heptafluorobutyric esters and quantified by electron capture GC on an 8 ft x 2 mm column of 3 percent OV-17 on Gas Chrom Q at 225 C. Quantification was achieved with a detection limit of 1-10 ng.

Benzo(a)pyrene-4,5-epoxide has been separated on a reverse phase Permaphase ODS column with a MeOH-H_2O gradient from 30:70 percent to 70:30 percent at 3 percent/min at 50 C. Identification was achieved by mass spectrometry, HPLC retention times, and UV analysis (89).

SECTION 4

GENERAL ANALYTICAL METHODS

The objective of this section is not only to provide a description of individual organic analytical techniques, but also to present a generally applicable analytical scheme which will be useful for either the quantitative analysis of grossly complex mixtures, or to seek specific organic species in complex mixtures.

An overall analytical strategy offering a maximum probability of successful qualitative and quantitative analysis of a complex organic mixture includes liquid chromatographic (LC) separation followed by determination of the compound classes present in the resultant LC fractions, and qualitative and quantitative analysis (90). Preliminary separation may be made by either conventional column chromatography or high performance liquid chromatography (HPLC).

Preliminary analysis will consist of screening each HPLC fraction by a combination of techniques such as infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectroscopy, and high-resolution mass spectrometry (HRMS). Having thus identified the classes of organic compounds which are present in each of the fractions, qualitative and quantitative analysis may be carried out by gas chromatographic-mass spectrometry (GC-MS), gas chromatographic-infrared spectroscopy (GC-IR), gas chromatography (GC), nuclear magnetic resonance (NMR), and high performance liquid chromatography (HPLC). HPLC in combination with NMR, IR, and mass spectrometry (MS) may be utilized exclusively for identification and quantification of very polar and ionic compounds, since these species are not amenable to separation by gas chromatography and have been largely ignored in earlier studies.

As can be seen in Figure 1, the separation into fractions and analytical screening will be iterative procedures, in so far as separation techniques will be reapplied as extensively as necessary until the screening techniques indicate that the complexity of each HPLC fraction is sufficiently reduced to permit qualitative and quantitative analysis.

SEPARATION BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

In order to successfully separate and analyze a very complex mixture, the use of multiple chromatographic techniques, or sequential analysis, may be necessary (Figure 2). The use of high performance liquid chromatography (HPLC) allows sequential analysis to be performed more quickly and efficiently than conventional column chromatographic techniques.

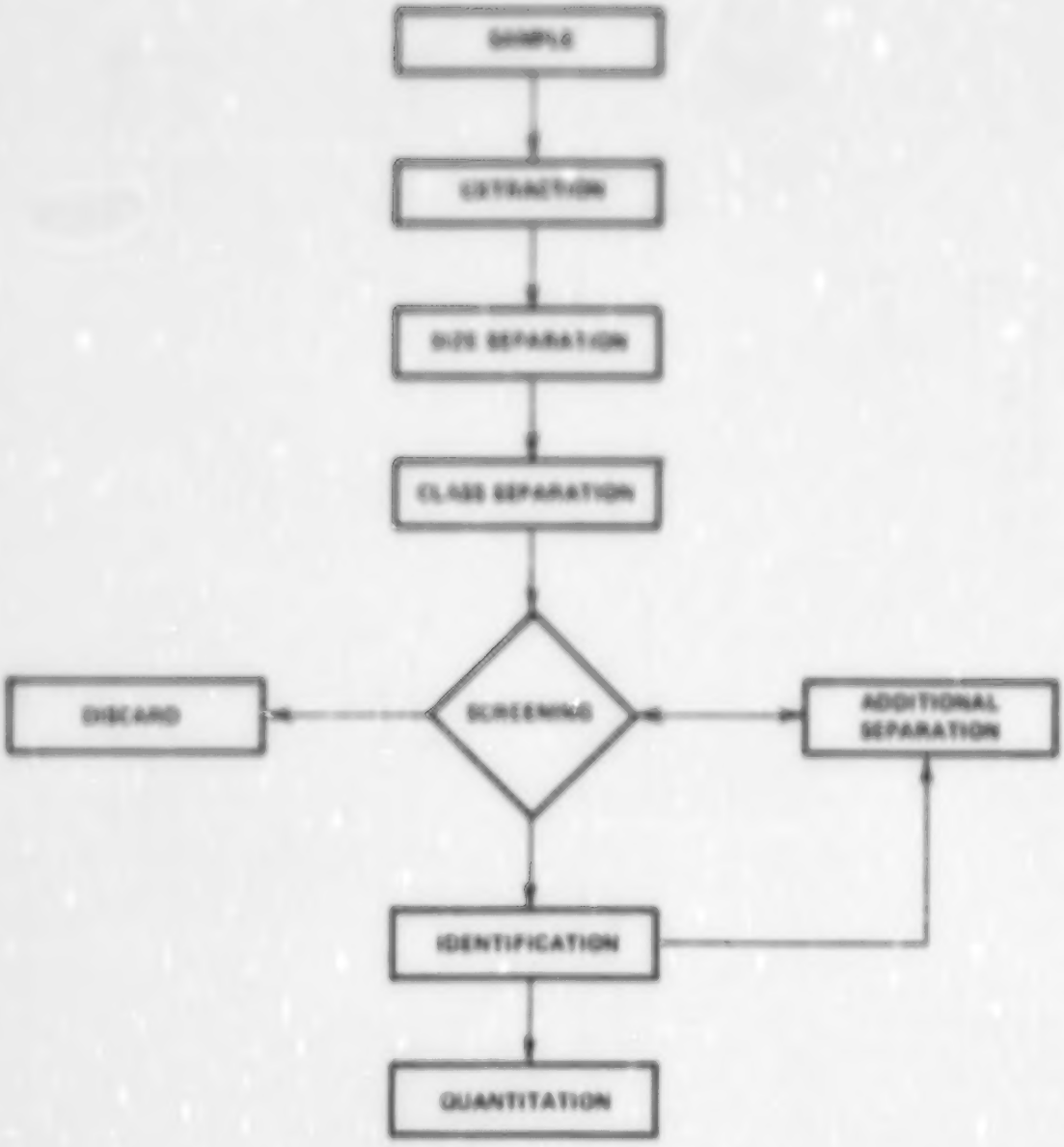


FIGURE 1. OVERALL ANALYTICAL STRATEGY

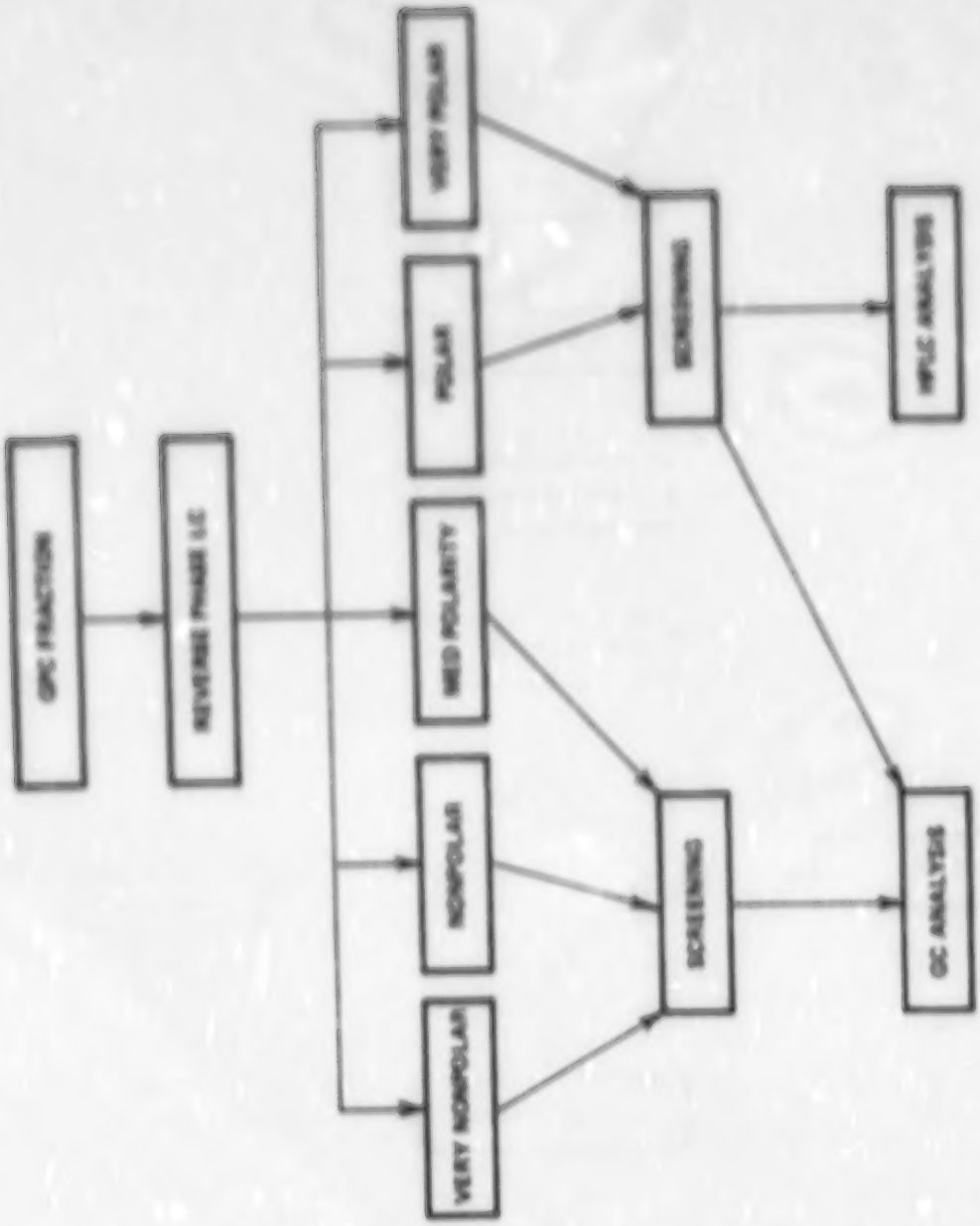


FIGURE 2. SEQUENTIAL SEPARATION - REVERSE PHASE HPLC

Separation by Size

The first step in the separation of a complex mixture is to separate by size or molecular weight, using gel permeation chromatography (GPC). GPC is an exclusion technique in which retention is based on a molecule's ability to penetrate the pores of the chromatography support. Figure 3 illustrates the principles of gel permeation chromatography. Large molecules elute with the solvent front while small molecules totally permeate the support and elute later. Within the range of elution volume, molecules can selectively permeate the support and thus be separated. Supports must be chosen for the exclusion limits that correspond to the molecular weight range that one desires to separate. For more detailed information, the following books and review articles should be consulted (91,92,93).

There are several advantages in using GPC as an initial separation method. A knowledge of the molecular weight of an individual fraction can dictate the choice of further separation steps such as gas or liquid chromatography as discussed subsequently. Narrow molecular weight ranges also allow simpler interpretation of the class separations that follow. Finally, information concerning molecular weight is useful for final identification purposes.

Gel permeation chromatography is the simplest form of high-performance liquid chromatography. Its use will divide a complex multi-component sample into manageable fractions. Once Step 1 of sequential analysis is completed, samples can now be further separated by class.

Separation by Class

In the previous section, we have seen how narrow molecular weight fractions could be obtained from a complex mixture by separation on GPC columns. The GPC fractions can now be further separated according to polarity by bonded phase liquid chromatography.

Bonded phase liquid chromatography is a form of liquid partition chromatography in which the stationary liquid is permanently chemically bonded to the support. Although the mechanism of retention is no longer strictly partition, bonded phases possess distinct advantages over liquid-liquid systems. Since the stationary phase is bonded to the support, it cannot be stripped off by the eluent and therefore precolumns are not necessary. More importantly, gradient elution, an extremely important technique which will be discussed shortly, can be performed with a wide choice of solvents. Finally, a wide range of selectivity can be obtained by the proper choice of chemically bonded phase.

In this second step of sequential analysis, a reverse phase bonded support should be used. It has been shown that for similar solutes, a plot of the log of retention time versus water solubility yields a straight line, when using reverse phase columns with water-methanol mixtures as the mobile phase (94). Since we have already obtained fractions of narrow molecular weight, it can be assumed that retention will be roughly a function of the particular functional groups attached to the molecule. We can therefore

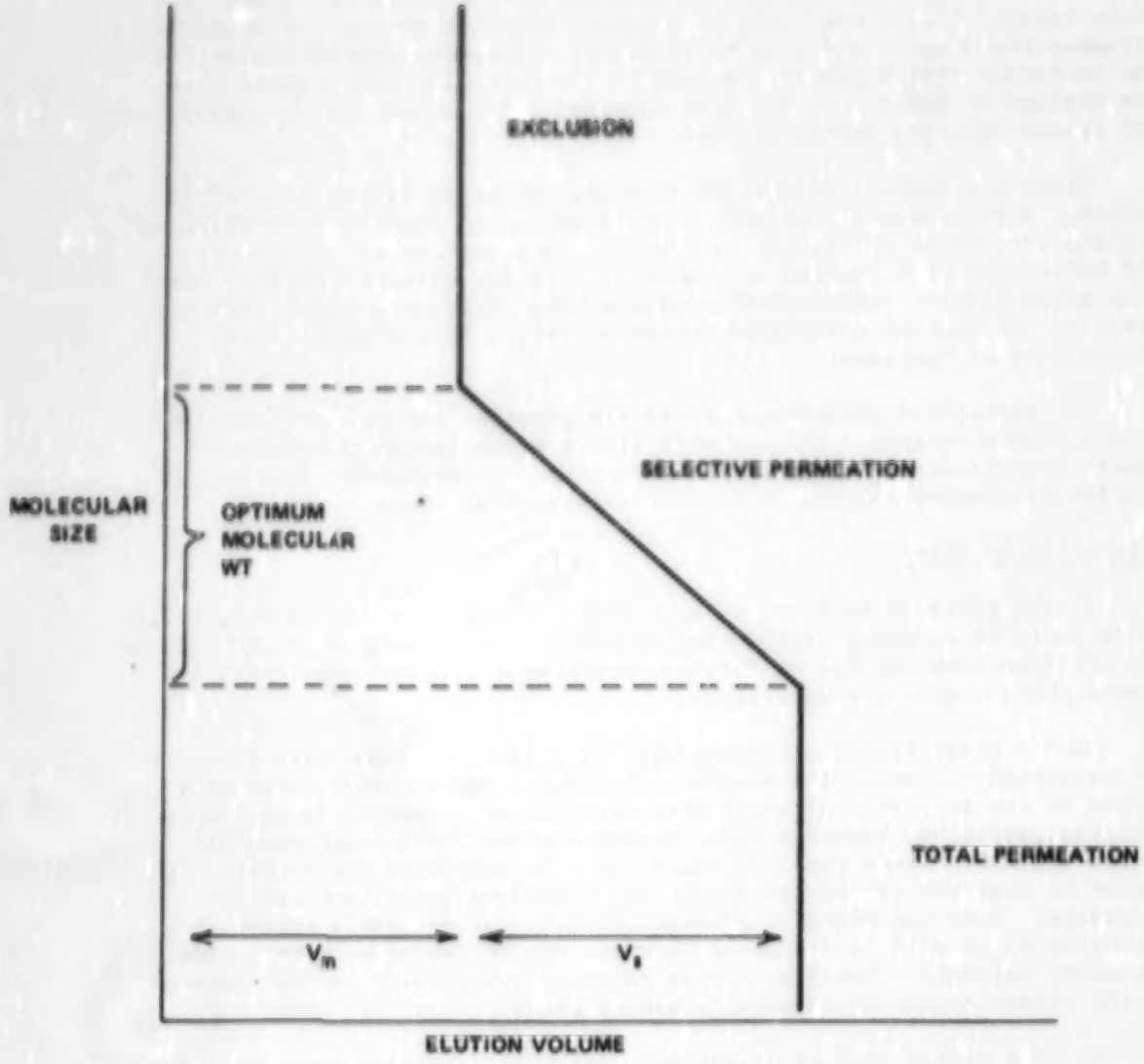


FIGURE 3. PRINCIPLES OF GPC

obtain a rough class separation by performing gradient elution on high-performance reverse phase column.

Functional Group Separation--

The fractions obtained from GPC can be further separated by reverse phase HPLC using gradient elution. Figure 2 shows, once again, a rough guide to the kind of separation one might expect. Very polar compounds will elute first and very nonpolar compounds will elute last. The fractions which are collected during this run may contain 1 or 2 components in a simple case of 100 components in an extremely complex mixture. However, these fractions should be sufficiently homogeneous to be screened by spectroscopic techniques for classes of organic compounds. If screening techniques indicate that a fraction contains compounds amenable to GC analysis, this route should be taken. Complex mixtures or mixtures containing compounds which cannot be run by GC should be further separated by HPLC. Large ranges in solvent composition are given to account for the molecular weight differences in a given class of compounds. For example, naphthalene and coronene might be expected to elute towards the two extremes of the POM range. Relative retentions for standard compounds of interest should be determined prior to unknown analysis so that narrow fractions can be obtained from the gradient run.

After Step 2 of this sequential analysis, a considerable separation of the samples has been accomplished and effective screening techniques should now be used to determine further cause of action.

SPECTROSCOPIC SCREENING TECHNIQUES

Separation of the sample into organic classes by HPLC will provide fractions which can be screened for complexity and/or types of compounds which are present. Identification of individual components is not intended in a screening technique, but rather the ability to discern the presence or absence of interferring compounds in a given class, and to judge the overall complexity of the mixture. In the case of the most complex mixture, screening will provide an indication of the type of separation needed to further fractionate the sample. For simple mixtures, screening will be a step toward qualitative and quantitative analysis.

The most useful technique used for screening is undoubtedly infrared spectroscopy, although nuclear magnetic resonance spectroscopy and high-resolution mass spectrometry may additionally prove to be effective.

Infrared Spectroscopy

Infrared spectroscopy has been, and still is, the most widely used tool for identification of organic compounds. One of the major uses of infrared spectroscopy (IR) has been screening during the separation of complex organic mixtures. It has provided functional group (especially on polar groups) identification in such mixtures, it has been used to monitor or screen the course of separation of the mixture, and ultimately it has been used to identify the compounds present when the separation has resulted in sufficiently simple mixtures. As with most analytical tools, less information is obtainable when the mixture was very complex as compared to when the mixture

was separated into smaller fractions. Now, however, the use of Fourier Transform infrared systems (FT-IR), has clearly demonstrated that a major increase in sample information can be obtained - even on complex mixtures - through the use of the FT-IR dedicated computer to do spectral arithmetic.

Thus, as separation techniques are applied, IR should be used to monitor the separation and identify the separated classes of species. Spectral subtraction should be used to magnify the differences between the separated fractions. Whenever possible, this spectral arithmetic will be used to minimize the need of chemical separations.

Used in this manner, IR will provide a major source of structural information to evaluate the HPLC separation and to determine whether or not more such separations are needed. When the IR data are combined with NMR data even more information can be obtained. Combining IR and NMR with good separation techniques and subsequently with GC-MS and GC-IR, utilizes the most powerful tools available for organic compound identification.

Fourier Transform Infrared Spectroscopy--

Fourier Transform infrared systems (95) differ from conventional dispersive infrared spectrophotometers in that conventional infrared spectroscopy uses a monochromator to generate the spectral information whereas an interferometer is used for this purpose in Fourier Transform infrared spectroscopy. The use of an interferometer to generate spectral information in the form of an interferogram (light intensity versus time) necessitates a second difference between the two types of infrared spectroscopy. This difference is that FT-IR systems use a dedicated digital computer to obtain the Fourier Transform of the interferogram, converting it to a conventional infrared spectrum (light intensity versus wavelength or frequency). These two differences lead to the following two major advantages of FT-IR over conventional infrared spectroscopy:

- Using an interferometer results in a substantial gain in energy or light throughput as compared to a monochromotor. This gain in energy results from the elimination of the dispersive device since all wavelengths of light are examined simultaneously in an interferometer and no energy is lost (as in a dispersive instrument by examining the light one wavelength at a time). This additional energy can be used in one of several ways: (a) for faster scan speeds (as fast as 0.6 sec), (b) for up to a 30-fold increase in signal-to-noise ratio, and (c) for 10^2-10^3 greater sensitivity.

- The availability of a dedicated computer offers several major data-handling advantages. Not only can spectra be ratioed against each other to remove absorption bands due to background materials, but the computer can be used to perform spectral arithmetic. Thus, spectra can be added or subtracted from each other and also multiplied or divided. In this way, the spectra can be adjusted in size, and unwanted components can be removed from the spectra without the necessity of chemical separation. This ability

to utilize a computer is not unique to Fourier Transform spectroscopy, i.e., in theory a computer could be attached to a conventional dispersive infrared spectrophotometer. However, in practice, this is rarely done, whereas all Fourier Transform systems use a computer. Thus, from a practical standpoint, the use of a computer is a major advantage in FT-IR systems.

Nuclear Magnetic Resonance Spectroscopy

NMR as a Screening Technique--

Nuclear magnetic resonance spectroscopy (NMR) is a powerful screening technique for mixtures of organic compounds. Although not used extensively in the past for analysis of mixtures, recent progress in instrumentation to improve resolution, stability, and sensitivity has made the observation of components of a mixture practical. The types and relative amounts of various functional groups in the mixture can be determined, and types of hydrocarbons can be identified. As a screening technique, NMR not only characterizes the general nature of the fraction, but also provides sufficient information to determine the types of further separations required.

The presence of various functional groups and identification of the types of hydrocarbons is determined from the chemical shift of peaks in the spectrum. This is due to the fundamental principle of NMR that the same nucleus in a different chemical environment resonates at a different frequency. A comprehensive listing of chemical shifts for protons and for other nuclei as well as a general review of NMR in the analysis of organic compounds is available from a number of sources (96-100).

The recent advances in instrumentation have extended NMR such that less abundant nuclei can now be routinely observed. The greatest growth has been in ^{13}C NMR. Carbon is of extreme importance due to its fundamental role in the structure of organic compounds. The carbon backbone of a compound and nonprotonated functional groups containing carbon, such as carbonyls or nitriles, can now be observed directly. Proton NMR and ^{13}C NMR together cover almost all organic compounds, making the combined methods a powerful screening technique for mixtures of organic components. ^{13}C NMR has an additional advantage over proton NMR. Since the shift range for carbon is 600 ppm compared to less than 20 ppm for proton nuclei, there is an enhancement in effective resolution. Broad envelopes of overlapping peaks in proton NMR may many times be resolved into individual carbon resonances. This allows for ready identification of specific functional groups. For a review and further discussion of ^{13}C NMR see References 101-105.

The preliminary limitation of NMR is sample size. For conventional continuous wave (CW) NMR, milligram quantities are needed for proton NMR, and natural abundance ^{13}C NMR is essentially impossible. This has largely been overcome by the use of Fourier Transform NMR. Unlike CW NMR, which slowly sweeps the radio frequency (RF) applied in a fixed magnetic field, Fourier Transform (FT) methods used short bursts of RF power at a discrete frequency for rapid data acquisition. The observation of spectra is made after the RF power is turned off. In this mode, data are generated as free induction decay patterns (signal intensity versus time). This multichannel excitation and detection results in a hundredfold improvement in

sensitivity. For proton NMR in the pulse Fourier Transform mode, a practical minimum is 10 μg of sample. For ^{13}C NMR, milligram quantities are required. Spectra of smaller amounts may be obtained by using microtechniques. The availability of a dedicated computer also provides the opportunity for data handling such as spectral arithmetic. The spectra can be adjusted in size and unwanted components can be removed by subtraction without the necessity of chemical separation. For a detailed discussion of FT-NMR, see Reference 105.

Evaluation of Screening Data

Determination of the complexity of a given HPLC fraction by the above-mentioned spectroscopic screening techniques leads to a decision-making point regarding whether the next step should be further separation, identification and quantification, or discard the sample due to lack of compound presence.

If the sample is of sufficient complexity or of mixed classes, further HPLC separations, as discussed subsequently must be performed prior to identification and quantification. Such a step would result in a recycling of the samples through HPLC separation and spectroscopic screening techniques until one class, a simple mixture of classes or a single component, suitable for identification and quantification, can be isolated.

If the screening procedures show the presence of only one class of compounds, a very simple mixture, or a single component, specific identification and quantification by one of the techniques discussed subsequently can be performed immediately.

In the case of a simple effluent sample mixture, several of the HPLC class separation samples may not contain any compounds. If spectroscopic screening procedures show a blank sample, then the fraction should be thus noted and the sample discarded without further analysis.

IDENTIFICATION AND QUANTIFICATION

Gas Chromatography (GC), and High Performance Liquid Chromatography (HPLC)

Introduction--

Gas chromatography is a powerful tool for separations of complex organic mixtures. In combination with selective detectors, particularly mass spectrometry, it is among the most powerful instruments available to the analyst. The principles of HPLC have been extensively discussed earlier, and thus only limited additional comments on its role in quantitative analysis will be made in this chapter.

A number of gas chromatographs are commercially available which are suitable for complex organic mixtures. It is important that the column oven is programmable at various rates up to about 400 C. The facility for dual columns and dual detectors is sometimes useful, especially when column effluent is split between two detectors such as a general purpose flame ionization detector (FID) and specific detectors such as a flame photometric detector (FPD) or electron capture detector (ECD).

The most important part of a gas chromatograph is the chromatographic column. There are various types of column ranging from packed, through support coated open tubular (SCOT), to high resolution capillary columns. Column packings include silica gel, alumina and polymers such as the Poropak and Chromosorb series, but the coated diatomaceous earth type are very commonly used. There are a great number of column packings commercially available; many of these have been developed in response to specific problems, whereas others have a more general usefulness. The listing given below in Table 1 does not pretend to be a complete inventory of column packings and coatings, but is presented to serve as a preliminary guide. Useful data may be frequently found in chromatographic supply manufacturers catalogues, in addition.

A significant proportion of GC separations may frequently be achieved using conventional packed columns. Capillary columns are becoming more widespread but their use requires greater skill than packed columns. The use of capillary columns in the analytical strategy presented here will be restricted to the separation of isomers and other groups of similar compounds, since many of the difficult separations will already have been accomplished by means of quantitative HPLC, which has been described earlier.

Gas chromatography can frequently provide good resolution of complex mixtures of organic compounds, and for this reason it is commonly used in organic analysis. An obvious limitation of the technique is that involatile materials are not amenable to this method of analysis. Involatile materials are most expediently analyzed by liquid chromatography, as described earlier.

A typical organic extract should normally be concentrated to a few hundred microliters, before subjecting one or two microliters to GC analysis. When an extract has been separated by HPLC, it is usual to concentrate this extract to about fifty to a hundred microliters prior to GC analysis. The choice of solvent for GC is not generally critical; commonly used solvents such as methylene chloride, acetone, or benzene generally elute significantly before any of the compounds of interest. If interference between solvent and sample peaks is observed it may be necessary to change solvents or GC columns.

The sensitivity of GC with conventional FID depends to a large extent upon peak sharpness and the level of noise or other interfering peaks. In the absence of appreciable interference, a sensitivity of 50 ng/µl may be reasonably obtained for hydrocarbons using FID. With FPD or ECD, for sulfur compounds or chlorinated pesticides for example, a sensitivity or between one and two orders of magnitude better than this is reasonably obtainable in most instances.

Quantification with GC and HPLC--

Gas chromatography is probably the most commonly used tool for quantification in organic analysis. High performance liquid chromatography has recently been used more extensively for quantification on account of significant improvements in instrumentation. In order to carry out quantitative analysis by either GC or HPLC, it is necessary that the compounds of interest should be reasonably well resolved from other peaks in the chromatogram. Furthermore, it is highly desirable that pure samples of the compounds sought

TABLE 1. ORGANIC SPECIES SEPARABLE BY VARIOUS GC COLUMN TYPES

Compound Type	Column Type
Acids C_1-C_9	Chromosorb 101
C_1-C_{18}	FFAP
Alcohols C_1-C_5	Poropak Q, Chromosorb 101
C_1-C_{18}	Silar 5CP, Carbowax 20M, FFAP
Polyalcohols	FFAP
Aldehydes C_1-C_5	Poropak N, DC-550, Ethofat
C_5-C_{18}	Carbowax 20M, Silar 5CP
Amines	Poropak Q/PEI, Poropak R
	Chromosorb 103, Pennwalt 223
Amides	Versamid 900, Igepal CO-630
Esters	Poropak Q, Dinonylphthalate
	Chromosorb 101 or 102
Ethers	Carbowax 20M, Silar 5CP
Freons	Poropak Q, Chromosorb 102
Glycols	Chromosorb 107
Halides	OV-210, FFAP
Hydrocarbons C_5-C_{10}	OV-101, SE-30
Aromatic	Silar 5CP, Carbowax 20M
Olefins C_6-	DC-550, DC-703
POM	Dexsil 300, OV-101, SE-30
Ketones	Poropak Q, Chromosorb 102, FFAP
Pesticides	OV-101, OV-225, OV-1, OV-17, SE-30
Phenols	OV-17, Silar 5CP, Carbowax 20M

should be available; if the components sought are not available, an approximation may be made through use of their analogues. An internal standard, or standards, must be chosen which will elute reasonably close to the peak(s) of interest, and will itself be free from interference from other chromatographic peaks.

Calibration is carried out by preparing a known mixture of internal standard(s) and compounds of interest, and obtaining a chromatogram for several different amounts of the mixture. The response factor for each peak may be determined by measuring height, area, or preferably by use of an automatic integrator or computer integration routine. Sufficient calibration chromatograms are run until a consistent response ratio between the internal standard(s) and the chromatographic peaks of interest is obtained. When response ratios between every compound of interest and an internal standard have been satisfactorily determined, the appropriate internal standards are added to the unknown mixture in amounts which are estimated to be of the same order of magnitude as the peaks which are being determined. GC analysis of the complex mixture plus internal standards is now carried out using the same chromatographic conditions at which the response ratios were originally obtained; from the response factors for the compounds sought in the complex mixture, and for the known amounts of internal standards together with the previously determined response ratios, the absolute quantity of each of the compounds sought in the complex mixture may be readily determined.

When the use of specific detectors, such as GC-ECD for halogenated pesticides, GC-FPD (sulfur specific filter) for sulfur compounds, or HPLC-fluorescence for POM compounds, quantification without obtaining good peak resolution on the chromatogram is often possible. This may be feasible because the sensitivity of the specific detector is very low for all but the compounds of interest, which permits previously interfering peaks to be neglected on the specific detector chromatogram.

The internal standards chosen for GC and HPLC quantification are usually similar in nature to the compounds which they are being used to determine, although this is not always mandatory. For example when carrying out GC quantification of POM species in combustion emissions an uncommon alkylated or phenylated POM compound is often chosen as an internal standard; it is of course important that the standard chosen does not occur in the complex mixture under analysis. In the GC analysis of C_{12} to C_{26} hydrocarbons from an oil-spill sample, it is not uncommon to add an absent C_{32} hydrocarbon to serve as internal standard for the mixture. When the highest accuracy is not sought, it is an accepted practice to assume that the chromatographic response for each member of a class of compounds is the same. Thus the POM compound 9-phenylanthracene could be used as an internal standard for all other POM compounds, each being assumed to have the same response as the internal standard, and the response ratio of each compound to the internal standard equal to unity.

The accuracy and reproducibility of GC and HPLC quantification using internal standards is generally better than $\pm$10%. The reproducibility may be readily determined while obtaining the response ratio calibration for each compound sought.

Gas Chromatographic-Mass Spectrometric Analysis (GC-MS)

Gas chromatographic-mass spectrometry is presently a widely used and powerful tool for organic analysis. Common practice is to interface a GC-MS system with a dedicated mini-computer, and a variety of output units such as a CRT teletype, or XY plotter, and a high-speed line printer. The GC-MS analysis contemplated in this report could not be accomplished without an interfaced mini-computer.

Electron Impact and Chemical Ionization--

Mass Spectra may be obtained by electron impact ionization (EI) or by chemical ionization (CI); in the latter mode, sample ionization is accomplished by means of an ionized reagent gas. In CI GC-MS analysis, the reagent gas, such as methane or isobutane, is most commonly introduced through its use as the GC carrier gas, no molecular separator being used at the interface between the GC and MS. The MS source pressure for CI with methane, for example, is typically as high as 600 microns, and thus the far higher concentration of methane than sample in the source ensures that sample ionization will occur exclusively by collision with ionized methane. Chemical ionization results in a rather different mass spectrum to electron impact in view of its being a much lower energy process; CI spectra are characterized by less extensive fragmentation of the molecular ion, and the fragmentation which occurs generally proceeds through loss of neutral molecules and appreciably more stable fragments than is the case with EI. (106) It is usual to observe a protonated molecular ion in CI and this is frequently accompanied by two adduct ions at M+29 and M+41, in the case of methane CI, caused by the addition of C_2H_5 radicals in the source of the mass spectrometer. Such adduct ions are generally diagnostic for the protonated molecular ion, and thus it is frequently possible to quickly assign a molecular weight during CI GC-MS analysis.

Since CI analysis is still relatively new, EI analysis maintains a significant advantage which is well suited to the analysis of complex organic mixtures. Over the past few years extensive data files of EI spectra have been built up, many of these give particular emphasis to toxid and hazardous substances. As yet, no comparable files exist for CI spectra. Data files of 40,000 or more EI spectra with which to carry out spectral matching as an aid to identifying unknown compounds are common. Spectral matching is often carried out by gaining access to spectral files in a central computer, with several laboratories sharing the same data file. In our experience, a very convenient method is to store a spectral matching data file on disk, and by means of a dual disk drive assembly interfaced with the GC-MS mini-computer it is then possible to carry out instantaneous spectral matching in the GC-MS laboratory. In any case, spectral matching is a very useful aid to the interpretation of known DI mass spectra, although it will often fail to suggest an immediately satisfactory spectral fit. Spectral matching often provides a useful guide which when coupled with other analytical data, such as a molecular weight from a CI mass spectrum, liquid chromatography separation data, and NMR and IR screening studies; correlation of such combined data can frequently lead to a reasonable interpretation of the mass spectrum.

Correlation with Separation and Screening Data--

GC-MS analysis does of course presuppose that the complex mixture subject to analysis is capable of separation by gas chromatography and an obvious limitation is compounds which are too polar to be satisfactorily separated by GC. Such compounds may be routinely analyzed by HPLC, as discussed earlier. A great deal of valuable data on an unknown sample will be obtained by screening studies even before GC-MS analysis is attempted, and the complexity of the mixture will have been significantly reduced by the HPLC separation scheme which has been discussed previously.

HPLC will initially be used to separate a complex mixture into three to five fractions by GPC on the basis of molecular weight, and then each of these size fractions will be separated into as many fractions as appears desirable by silica gel or reverse phase HPLC in order to provide relatively simple mixtures for the subsequent stages of analysis. Following the complete HPLC separations, probably into about 20 fractions, screening studies using IR, NMR, and GC will have been carried out as appears appropriate.

Each fraction of the complex mixture of a given molecular weight range will be separated by HPLC on the basis of polarity into a number of well resolved fractions. The very nonpolar fractions will consist of aliphatic hydrocarbons and will not be subject to GC-MS analysis, since these species are more efficiently analyzes by GC alone. The most polar fractions from the HPLC separation scheme will be unsuitable for GC separation on account of their high polarity and involatility, and will be characterized by further HPLC separation together with IR, NMR, and low resolution MS as required. However, the HPLC fractions in between these two extremes will range from nonpolar POM species to polar polyfunctional compounds, and these will be identified by GC-MS (and possibly GC-IR) preceeded by extensive screening of each HPLC fraction by the other analytical techniques as discussed earlier.

Whether CI or EI mass spectra, or both, are obtained will depend to a large extent on the information available from the preliminary screening and HPLC separation data. For fractions containing the POM species, there is little point in obtaining both EI and CI spectra, since fragmentation is almost negligible and uniformative in both cases. However, the preliminary screening data will make it clear that POM species are present, and CI mass spectra will provide molecular weights which when coupled with chromatographic data will permit unambiguous compound identification.

For HPLC fractions containing monofunctional compounds, such as aldehydes and phenols, CI mass spectra may frequently provide sufficient screening analysis. For example, if an HPLC fraction is known from screening to contain primarily aromatic aldehydres, it should be relatively straightforward to assign benzaldehyde, tolualdehydes, and higher alkyl benzaldehydes from the CI spectra, since the only prominent fragmentation will be loss of 28 mass units for CO, to leave the carbon skeleton. The mass spectra are unlikely to give guidance regarding isomers, but this information may be inferred from chromatographic data, or possible GC-IR data.

For HPLC fractions which contain polyfunctional compounds, or a mixture of compounds of different functionality, the most expedient approach in

GC-MS analysis would be to initially run EI spectra, and initially rely upon spectral matching, and fragmentation interpretation, to suggest some possible structures for the compounds present. The available screening data will greatly assist in narrowing the choice from the list of spectral matches. It may not at this stage be possible to make a good assignment of some of the compounds present, and it would probably be most helpful to additionally obtain CI mass spectra. The CI spectra would further narrow the possibilities by providing a probably molecular weight for the compounds of interest, and the CI fragmentation may give further valuable data necessary to arrive at a structural assignment. CI fragmentation for moderately polar species can be rather more informative than for less polar compounds, since the greater charge separation in the molecule may be more likely to promote fragmentation; for the same reason, EI fragmentation of very polar species may often be too extreme to be of much value.

GC-MS Data Analysis--

The basic routines available with all commercial mini-computers for GC-MS are 'RGC' (reconstructed gas chromatogram) and a mass spectrum printing routine. Modifications of the RGC routine are invaluable for the location of minor chromatographic peaks. The normal RGC plot consists of a reconstructed chromatogram which contains ions of all mass numbers, see for example the 'total ion chromatogram' in Figure 4. In order to locate the GC peak for a compound whose mass spectrum is known, RGC plots containing prominent ions in the mass spectrum of this compound may be made. These RGC's should be overlaid upon the original total ion RGC, maxima in the RGC specific ion overlays will occur at the spectrum number corresponding to the compound of interest in the total ion RGC.

For example, Figure 4 shows a portion of the GC-MS analysis of residual oil combustion effluents. In this case, the sample extract was subjected to liquid chromatography on silica gel to isolate the hydrocarbon and POM species. Several individual ion overlays are shown superimposed upon the total ion chromatogram. The 253 ion overlay shows maxima at spectrum numbers 166 and 179, although it is apparent that no peaks are visible on the original total ion chromatogram. If the spectra at spectrum numbers 166 and 179 are displayed or printed out, it is evident that these two peaks are benzfluoranthene or benzpyrene isomers; the spectra are both characterized by a base peak at m/e = 253 (M+1) and adduct ions (M+29, M+41) at m/e = 281 and m/e = 293 as shown in Figures 5 and 6. In practice, spectrum 167 minus spectrum 162, and spectrum 179 minus spectrum 169 would be displayed in order to subtract any spurious background ion peaks due to column bleed, and the tailing from other chromatographic peaks. The presence of the compound sought should be confirmed by printing out its mass spectrum in this manner, since spurious 'hits' sometime occur due to interfering fragments from other compounds.

GC-MS Quantification (Specific Ion Monitoring)--

GC-MS analysis offers a highly selective and sensitive mechanism for the quantification of compounds which have been identified on a complex mixture (107). Quantitation of an identified material of interest may be expediently carried out by measurement of one or more characteristic ions in the mass spectrum of the material. From the standpoint of both sensitivity and

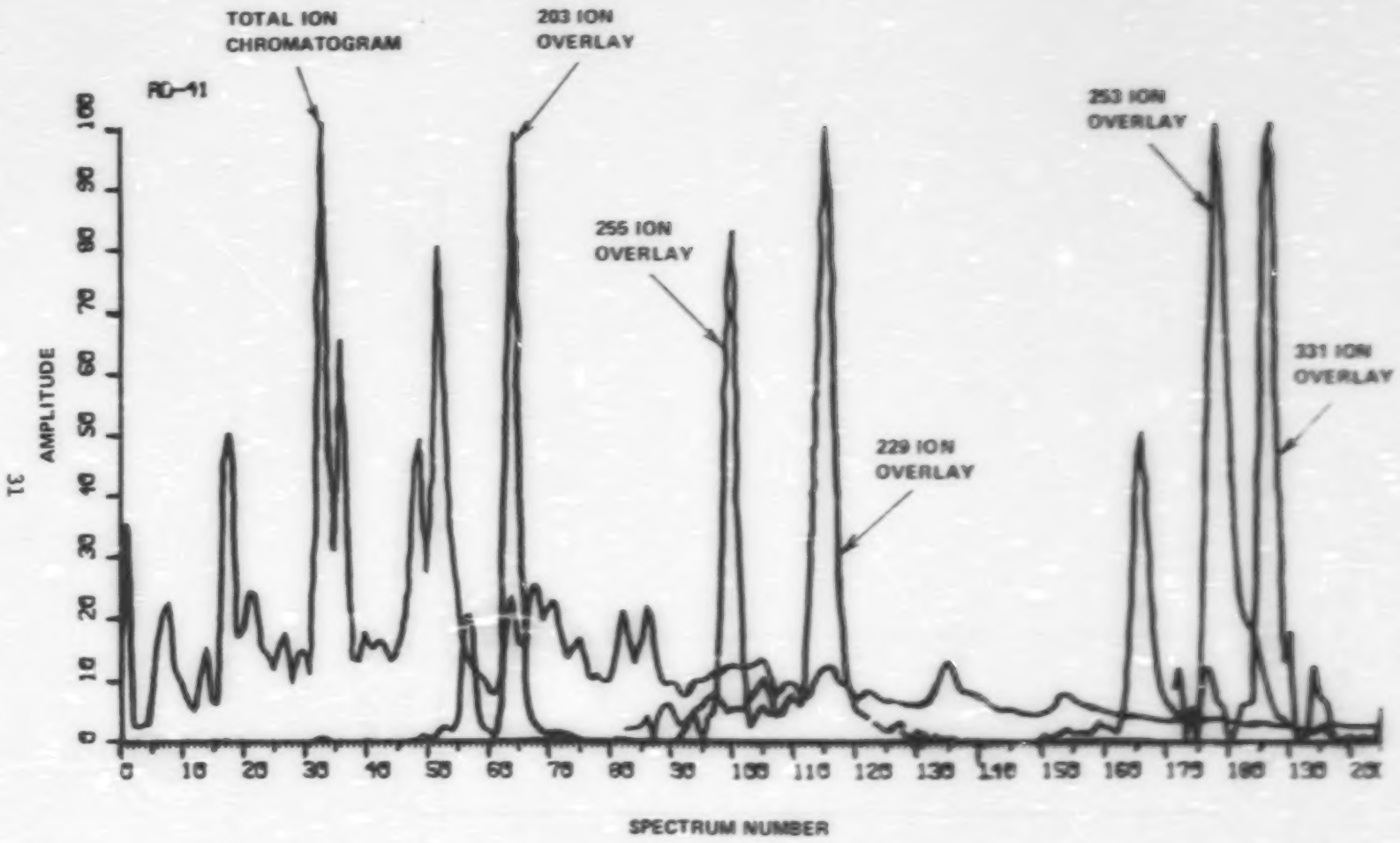


FIGURE 4. RECONSTRUCTED ION CHROMATOGRAMS OF RESIDUAL OIL COMBUSTION EFFLUENTS

SPECTRUM 167-162

GC-MS (CH4) OF RESIDUAL OIL COMBUSTION EFFLUENTS

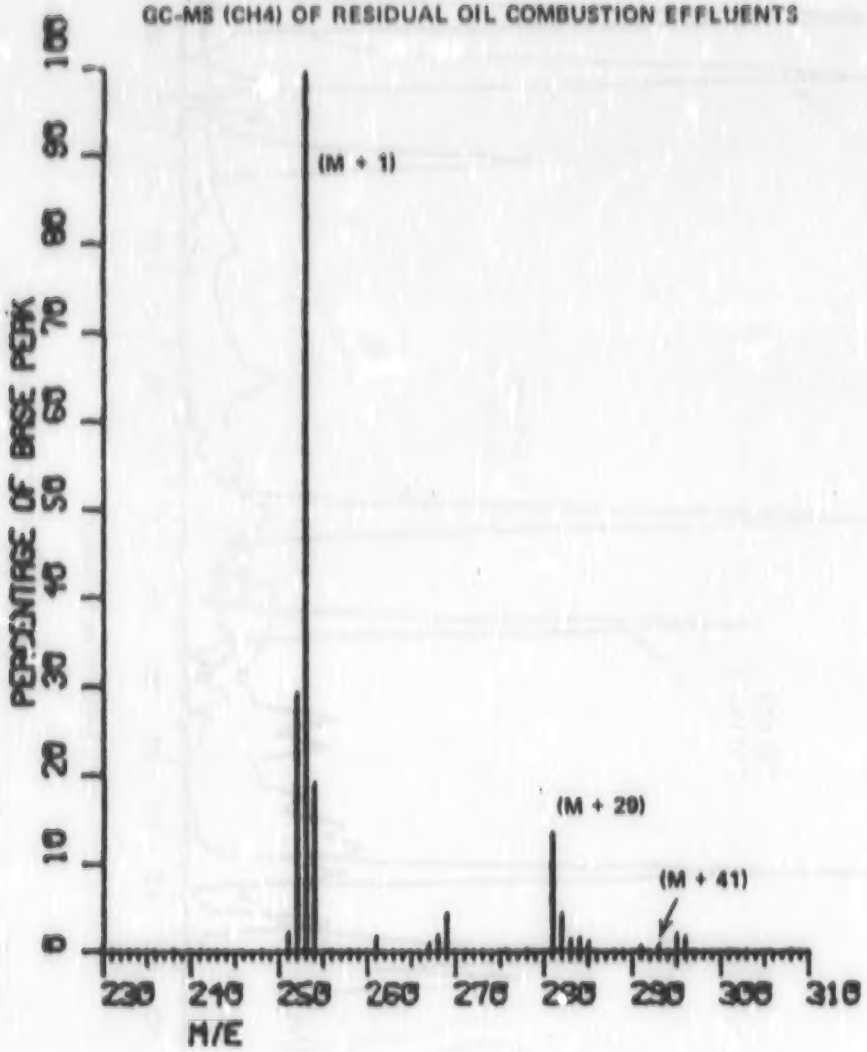


FIGURE 5. MASS SPECTRUM OF BENZFLUORANTHENES

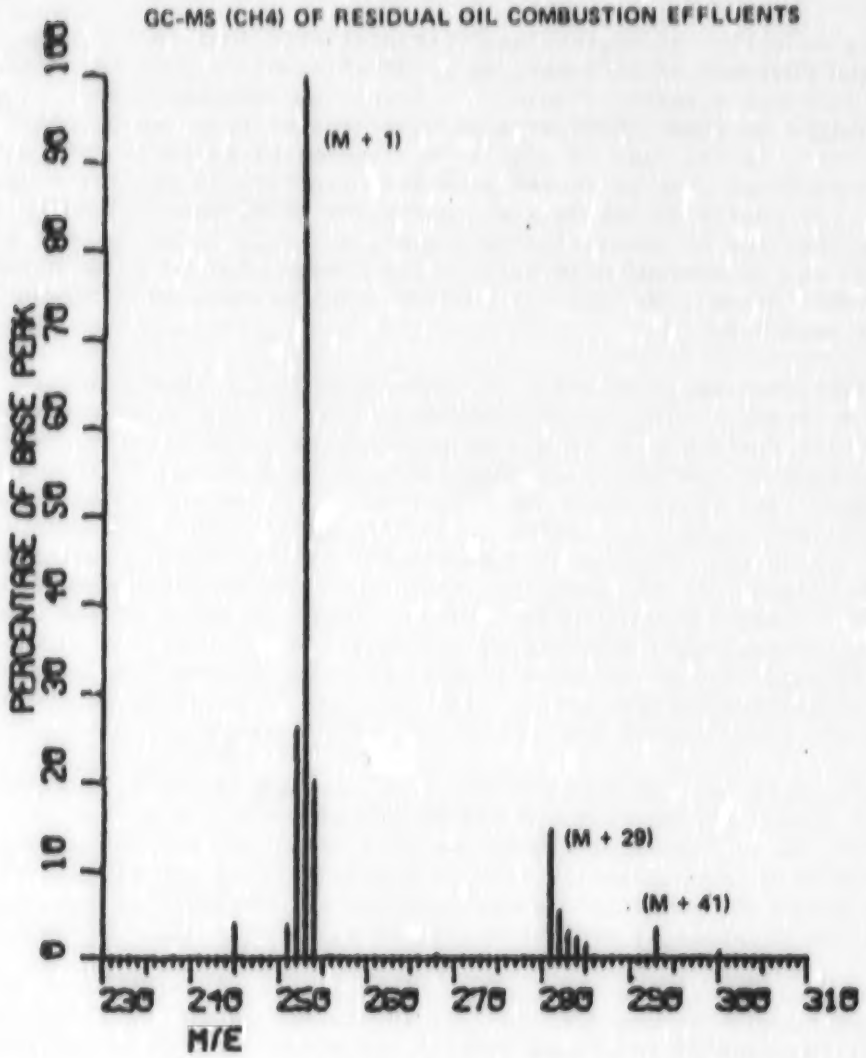


FIGURE 6. MASS SPECTRUM OF BENZPYRENES

selectivity, it is frequently an advantage to use chemical ionization, described earlier, in view of the far less extensive fragmentation of the molecular ion which results in a more intense ion (or ions) at high mass number.

Following selection of appropriate characteristic ions in the mass spectrum of the compound of interest, an internal standard must be selected. Ideally, the internal standard should be a deuterium labelled analogue, with a molecular weight at least three mass numbers greater than the sought species. However, in the case of complex environmental mixtures this is frequently impractical, and an isomer or other structurally similar compounds may be used. The choice of internal standards for GC-MS quantification is more exacting than for GC quantification, since not only do we require a compound which elutes conveniently near to the compound(s) to be measured, and is not itself present in order to obviate interferences from fragment ions of other materials.

Up to eight ions may ordinarily be measured during a quantitative specific ion monitoring (SIM) GC-MS analysis, although that number may be significantly increased by use of a computer program which permits changing the monitored ions at specific time intervals. Thus when the first set of sought compounds have eluted from the GC column, a second set of ions may be monitored; this technique is referred to as 'sequential SIM'. For the latter purpose, and for accurate location of qualitatively identified species in the mass chromatogram, it is highly desirable that the computer should be equipped with a real-time programmable clock. Quantification of the compounds of interest is subsequently achieved by ratioing the measured ion current of the sought compound to that of the internal standard, by applying a previously determined calibration factor, which allows for any differences in ionization efficiencies of this compound and the internal standard.

The sensitivity for SIM GC-MS quantification, and for GC-MS analysis in general, will always depend upon the nature of compounds being studies. For a compound such as an aliphatic dialdehyde with extensive fragmentation, and whose mass spectrum is necessarily weak, a sensitivity of 100 ng/µl can routinely be obtained, sensitivities of an order of magnitude or more higher than this may be obtained if mass spectrometer conditions are optimized.

One of the most useful analytical routines is spectral matching, as previously mentioned. We consider that it is preferable to use a dual disk drive whereby the bank of reference spectra are stored on a separate disk which is readily accessible during mass spectral analysis. Ideally, the RGC of a fraction from HPLC separation should be displayed on the CRT, and a queue of mass spectra corresponding to RGC peaks should be stored in the computer memory by command from the teletype. When the queue is established, the matching routine may be activated and a chosen number of compound matches (with correlation coefficients) for each RGC peak may be printed by a high-speed line printer.

Gas Chromatographic-Infrared Spectroscopic Analysis

While infrared spectroscopy (IR) is the most widely used analytical tool

for the identification of organic compounds, it has given way to mass spectrometry (MS) for the identification of organic compounds in vaporizable, complex mixtures. The reason for this was that the characteristics of mass spectrometry were well suited to coupling with a gas chromatograph (GC) so that GC could be used to separate the mixture and MS used to identify the separated compounds. The sensitivity and speed of MS was such that this could be done "on-line" or "on-the-fly". GC-IR studies used to require trapping and collection of each GC peak, and not only was this time consuming, but often there was not enough material available for this purpose.

With the advent of Fourier Transform infrared systems (FT-IR), "on-line" GC-IR became a reality. The extra energy throughput of the interferometer of the FT-IR system could be used to give complete infrared scans in as little as 0.5 sec. Thus, scanning speed was certainly fast enough for "on-line" GC-IR without the necessity for trapping and collection of the GC peaks. While the sensitivity level is not as low as desired, it is adequate for many samples. In addition designs are available for modifying the infrared light pipe used for GC-IR and this coupled with the use of a liquid nitrogen cooled infrared detector has been demonstrated to lower the sensitivity to 400 nanograms per GC peak. This sensitivity range makes it possible to obtain infrared spectra "on-the-fly" of most gas chromatographic peaks. Not only would such modifications be fairly easy to make, but a complete unit incorporating these changes should soon be commercially available.

Thus, GC-IR joins GC-MS as a routinely used instrument for the analysis of complex mixtures and will be an invaluable analytical tool for identification of the components separated by gas chromatography. It is important to appreciate that GC-MS and GC-IR techniques frequently complement each other. Since the bases for GC-MS and GC-IR identifications are fundamentally different, analyses using both techniques will provide substantially more compound identification data than either technique used independently.

Since the GC-IR system is fully automated, the sample is merely injected into the gas chromatograph and the FT-IR computer automatically scans, collects, and stores the interferogram for each GC peak. The operator then has to manually instruct the computer to plot out each spectrum. Identification is made by standard infrared procedures, that of matching the unknown spectrum with a reference spectrum from available reference libraries of up to 150,000 spectra. This can be aided by computer search systems. When an exact match (with a reference spectrum) cannot be found, the functional group information (available from the IR spectrum) can often be coupled with the MS data to uniquely identify an unknown compound.

SECTION 5

SAMPLING METHODOLOGY

INTRODUCTION

Sampling is perhaps the most critical stage in the measurement of hazardous organic species in stack gases; in the absence of a reproducible and quantitative sampling procedure, sophisticated and sensitive analytical procedures are of no value. The objective of this chapter is to examine the parameters necessary for the efficient collection of organic materials from stack gases.

There are several fundamental requirements of any sampling system for organic materials which are present in stack gases, if the subsequent analytical data are to be meaningful.

(1) Organic compounds of interest must be quantitatively collected

(2) The integrity of the collected sample must be preserved

(3) The sampling system must be amenable to quantitative sample recovery in a manner appropriate for subsequent analysis

(4) The capacity of the sampling system must enable sufficient sample to be quantitatively collected for whatever analytical technique is to be applied.

Either through lack of concern, or an inability to overcome technical difficulties, little progress has been made towards the development of a sampling system which would satisfactorily meet the above requirements.

Among the earliest collection methods employed were those which made use of filtration combined with impinger systems. While such techniques may give efficient collection of particulate, losses of organic vapors would appear to be inevitable. This feature was highlighted by Stanberg (108), who made use of a filter, impingers containing xylene, and cold traps, for the collection of combustion effluents, with special concern for benzo(a)pyrene. At high filter temperatures (>300 F) significant losses of benzo(a)pyrene were reported, but at cooler filter temperatures (<95 F) more efficient collection was reported. At the higher temperature range a substantial portion of the benzo(a)pyrene would be present on the vapor phase, while at the lower temperature particulate formation would be favored; accordingly,

much of the benzo(a)pyrene would be retained on the filter at low temperatures, but at the higher temperatures, both filter and the impingers were unable to effectively trap the vapor.

The most widely used impinger method for the collection of organic materials from stack gases has been EPA Method 5 (109,110), a technique designed for the collection of particulate material, which was first published in the Federal Register in 1971. Unfortunately, Method 5 was never intended for collection of organics; it has a poor efficiency for collection of vapors, and sample recovery is at best difficult. Nevertheless, a large number of organic measurement programs have been carried out on stack gases using this method; all of the data from these must unfortunately be regarded as questionable.

A recent program for the development of a method for sampling POMs and PCBs from combustion effluent led to a modified Method 5 utilizing xylene impinger cooled with dry ice (4). The prescribed technique for sample recovery from the impingers and filters extract would preclude accurate quantification, since this involved evaporation of the sample to dryness followed by redissolution in xylene. While removal of excess solvent from a sample extract always presents the risk of sample loss, evaporation of a sample solution to dryness will lead to significant loss of volatile organic materials. This sampling system was used on a study of the emissions of PCBs from incineration of domestic refuse (111); although other experimental difficulties prevented meaningful data from being obtained, no attempt was made to validate the sampling system.

Attempts have been made to collect stack gas samples through the evacuated containers or collapsible bags (112). Such methods will provide quantitative collection, but one characterized by large sample losses to the containers' walls. Another major drawback is the small volume of gas collected in this manner, which would result in very low analytical sensitivity.

REVIEW OF ACCEPTABLE METHODS-RECOMMENDATIONS

Within the last two years, a new concept in stack sampling for organic materials has come into increasingly common use. A combination of conventional filtration with collection of organic vapors by means of a high surface area polymeric adsorbent has proved highly efficient for collection of all but the more volatile organic species. The earliest sampling systems of this type were modifications of the EPA Method 5 in which the polymeric adsorbent was located between the heated filter and the conventional impingers. A typical example is the Battelle Adsorbent Sampling System, the Adsorbent Sampler of which is shown schematically on Figure 7. The stack gases are sampled isokinetically by a sampling probe and passed through a heated filter, as described in EPA Method 5. Immediately after leaving the hot filter, the emissions pass into the cooling coil (120 x 0.8 cm) of the adsorbent sampler and then pass through a Pyrex frit and into a cylindrical column of Tenax adsorbent (7 x 3 cm containing 12 g of Tenax for the Mark I sampler, 8 x 4 cm containing 25 g of Tenax for the Mark II sampler). The flow rate through the Mark I adsorbent sampler is typically 14 l min^{-1}, with a maximum of about 21 l min^{-1} (or 0.75 cfm). The Mark II sampler has a maximum flow rate of

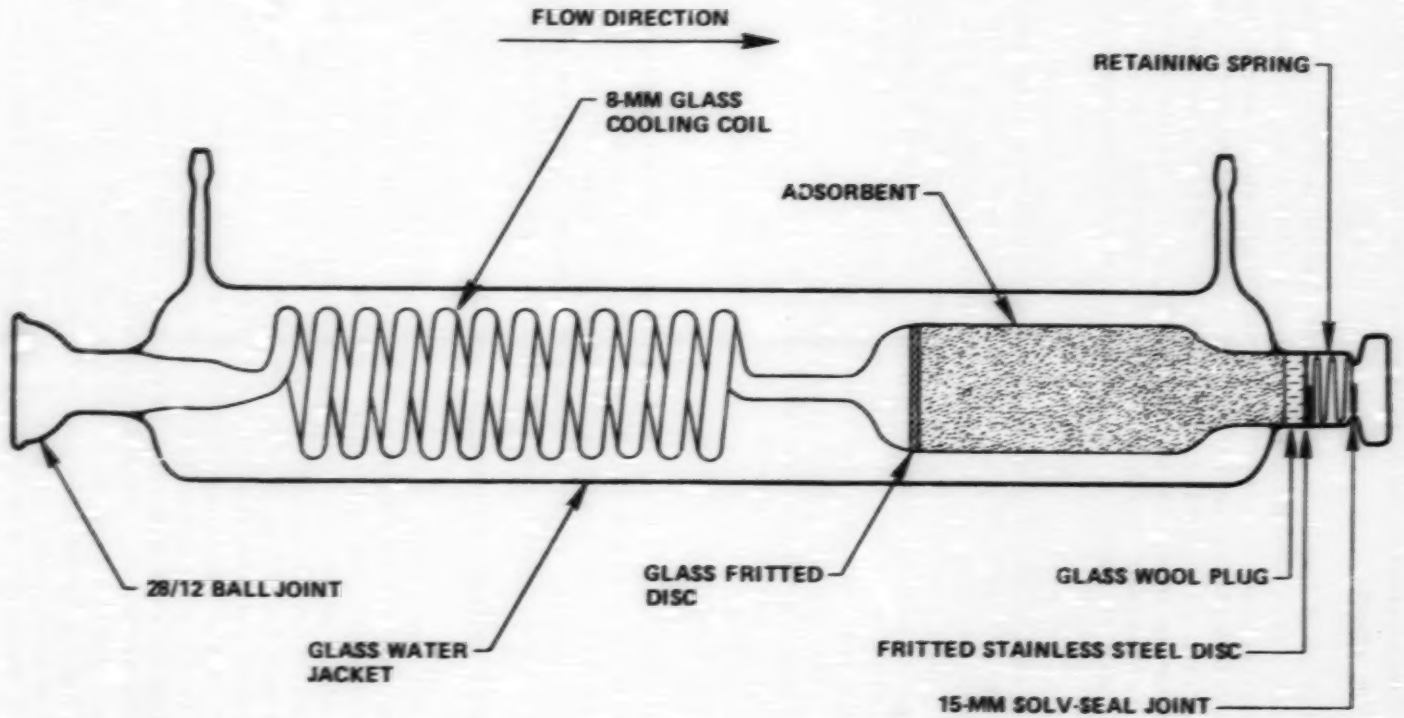


FIGURE 7. ADSORBENT SAMPLING SYSTEM

about 1.5 cfm. The cooling coil and Tenax adsorbent are maintained at a constant known temperature by means of a thermostated circulating water bath. The incoming gases are cooled to maintain adsorbent efficiency; yet, the adsorbent is maintained above ambient temperature to preclude condensation of the large quantities of water vapor present in all combustion effluents. The gases leaving the sampler are drawn through an aqueous impinger, a Drierite trap, and dry gas meter by a Gast-0522 vacuum pump (as in Method 5 sampling). Thus, essentially, the new adsorbent sampling system consists of the standard EPA train with the adsorbent sampler located between the filter and the impingers. With this system, filterable particulate can be determined from the filter catch and the probe wash according to Method 5, whereas the organic materials present can be determined from the analysis of the filterable particulate and the Adsorbent Sampler catch. The impingers are only used to cool the stream and protect the dry-gas meter, and their contents are discarded.

The Battelle Adsorbent Sampler was designed to collect sufficient sample for organic analysis; quantification of known species from stack gases may routinely be carried out at the ppt level, or lower, through use of an appropriate analytical technique. Although originally developed to facilitate quantitative measurement of POM species, recent laboratory validation studies have demonstrated that the Battelle Adsorbent Sampler can provide quantitative collection of wide ranges of organic materials including: PCBs, PCNs, epoxides, nitrosamines, chloralkylethers, lactones, methane sulfonates, carboxylic acids, and phenols (113). Furthermore, the latter studies have examined the effect of several important parameters on this sampling system, including nitrogen oxides, sulfur oxides, water vapor, sampler temperature, and sample loading; details of this work, which is applicable to other similar sampling systems, are discussed later.

In view of the apparent success of filtration-adsorbtion sampling systems for organic materials in stack gases, EPA (IERL-RTP) has recently developed the Source Assessment Sampling System (SASS) for the collection of particulate and volatile materials. This sampling system is described in detail in two recent EPA reports (114,115), but will be summarily included here.

The SASS train consists of a stainless steel probe which enters a thermostated oven containing three series cyclones and a filter holder. The cyclones facilitate collection of particulate in the following size fractions: >10 μm, 3-10 μm, 1-3 μm; a 142 mm filter collects the less than 1 μm particulate size fraction. Following the oven containing the cyclones and filter, volatile organic materials are collected in a sorbent trap containing XAD-2 resin; a vessel for the collection of any condensate is provided directly below the XAD-2 trap. After exiting the sorbent trap, the gases pass through an oxidative impinger system for the collection of volatile inorganic materials, before exiting the system through a 10-cfm pump and dry-gas meter. The EPA SASS train has a nominal flow rate of 3-5 cfm. A schematic diagram of the EPA SASS train is shown in Figure 8.

The EPA SASS train promises to be a particularly effective sampling system for source assessment studies, in view of the relatively large amount of material which may be obtained for both chemical analysis and bioassay

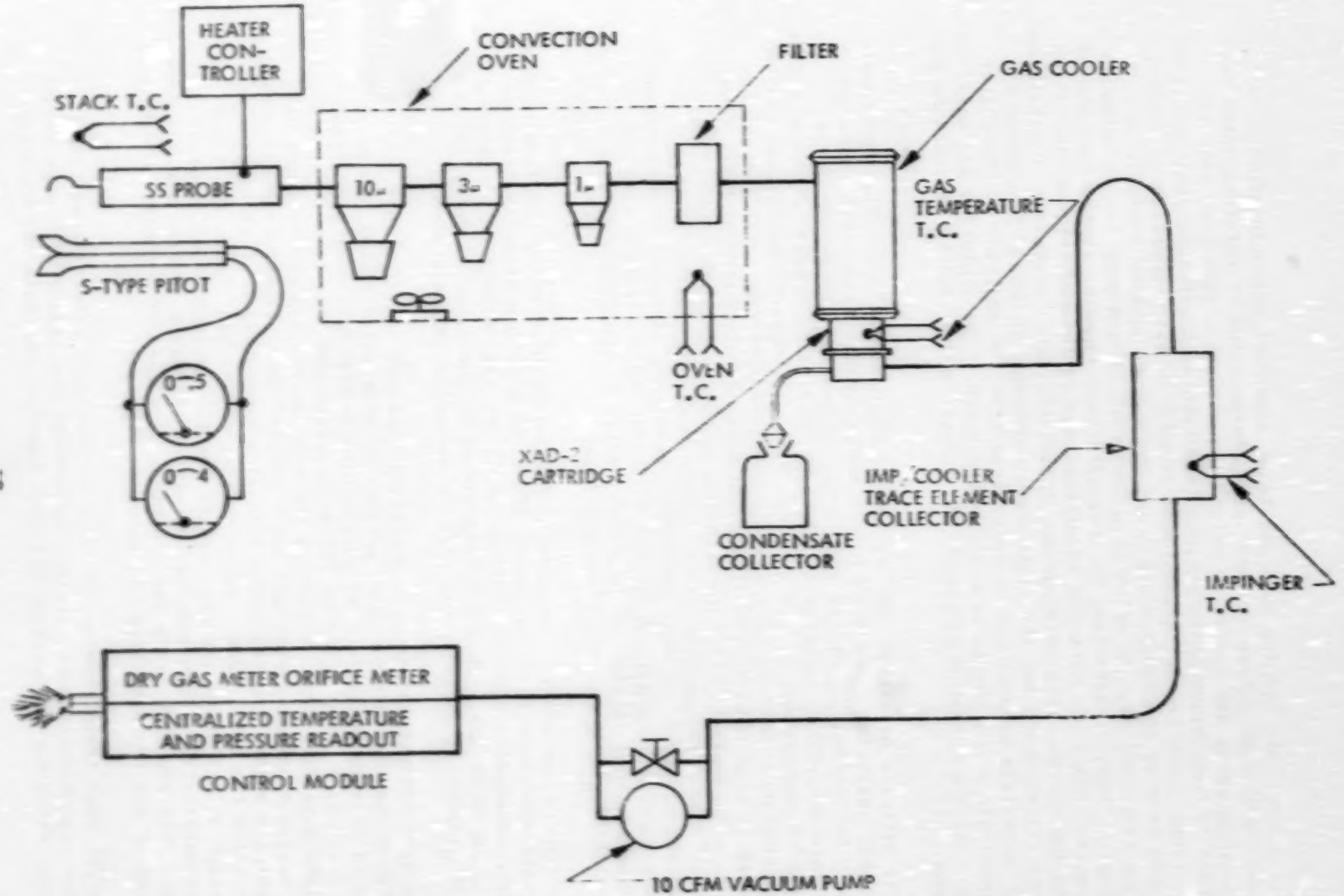


FIGURE 8. SOURCE ASSESSMENT SAMPLING SCHEMATIC

studies; it has been proposed that an acceptable sample size for the SASS train will be 30 scfm (114,115) which is equivalent to approximately 6-8 hours of sampling. Additionally, the size fractionation of the particulate material may permit the association of hazardous materials with a particular size range, which would provide valuable input to emission control strategies.

It should however be borne in mind that as of this report date, the entire SASS train is relatively untried, and lacks authoritative laboratory and field validation for collection of hazardous materials of concern. Validation data and acceptable operating parameters which have been obtained for the Battelle Adsorbent Sampler (113) will serve as a guide for operation of SASS XAD-2 sorbent trap until directly applicable data become available.

Very recent studies (116) have demonstrated that the stainless steel gas cooler and XAD-2 cartridge of the SASS train may cause sample contamination through interaction with the incoming gas stream. Subsequent field trials of a prototype pyrex gas cooler and XAD-2 cartridge which is interchangeable with other SASS components appears to have obviated this problem. Preliminary flow rate difficulties with the glass system have been overcome with the redesign as two separable units; the XAD-2 cartridge now incorporating two 90 mm glass fitted discs and facility for side-loading of the adsorbent resin.

Sample Recovery from Filtration-Sorbent Sampling System

All presently acceptable sampling trains for the collection of particulate and organic vapor consist of some combination of polymeric adsorbent traps, heated filters, and heated cyclones. Recovery of collected sample is achieved by extraction with a suitable solvent; generally applicable methods are described below.

Filters--

Extraction of filter material should be carried out initially with methylene chloride followed by a reextraction of the residue and filter with methyl alcohol in order to ensure that all polar and nonpolar organic material is efficiently recovered. Extraction may be carried out using a Soxhlet apparatus for 24 hours, or by ultrasonic agitation of the filter with solvent in a sealed glass container for 1 hour, followed by conventional filtration of the shredded filter and insoluble particulate matter. We have found both methods of extraction to be satisfactory, but support the report (117) that ultrasonic agitation may be slightly superior.

Cyclones, and Probe Rinse--

Particulate material which has been removed from a cyclone or rinsed from a probe may be solvent extracted in a similar manner to a filter. Soxhlet extraction may be carried out in a cellulose thimble plugged with glass wool, or in a fritted (fine) glass thimble with a glass wool plug. Ultrasonic extraction of particulate may be carried out by agitation with solvent in a sealed glass container followed by conventional filtration to remove the insoluble material.

Porous Polymer Adsorbent Traps--

The preferred method of solvent extraction involves continuous solvent extraction of the adsorbent for a period of 24 hours (118,119); alternatively, the contents of the adsorbent trap may be transferred to a cellulose extraction thimble, and subjected to 24 hours of Soxhlet extraction.

The choice of solvent for extracting a porous polymer adsorbent trap depends partly upon the nature of the adsorbent. It is important that the solvent chosen does not affect the adsorbent in any way, yet is still an effective solvent for the removal of collected material. For porous polymer adsorbent traps utilizing Tenax, we would recommend extracting with a hydrocarbon such as pentane followed by methyl alcohol. Porous polymer adsorbent traps containing XAD-2 resin should be extracted by methylene chloride followed by methyl alcohol. Extensive validation studies have demonstrated that Tenax is unaffected by extraction with the above solvents (113). Such validation studies are presently lacking for XAD-2, although preliminary solvent interaction experiments have demonstrated that the resin has negligible solubility in methylene chloride.

Liquids--

Aqueous solutions may be solvent extracted by means of conventional liquid-liquid extraction in a separatory funnel; methylene chloride will frequently prove to be a suitable solvent. Alternatively when the organic compounds sought are believed to have a reasonable vapor pressure (most compounds except the very polar), vapor displacement and adsorbtion may be used. Inert gas is bubbled through the liquid, and is then passed through a trap containing chromatographic adsorbent where the volatilised vapors are trapped (120). Sample recovery from the adsorbent may be made by extracting it with a suitable solvent, as discussed previously.

A further aqueous extraction procedure involves percolating the solution through a column of chromatographic adsorbent or resin (121), again followed by solvent extraction of elution of the solid to recover the organic sample.

Organic oils should not be extracted but should be directly subjected to high performance liquid chromatography.

Preparation of Extracts for Analysis--

The manner in which the various sample extracts are combined depends upon the information that is required from the emission source. It is possible that particulate and vapor may need to be analyzed separately on account of data required for an emission control strategy, for example. In any case, each extract or combination of extracts should be reduced to a volume of 0.5 ml or less by a Kuderna-Danish evaporator, the sample is then ready for direct analysis or separation into fractions by high performance liquid chromatography. While it is true that some of the more volatile species may be partly lost during this procedure, the sampling techniques utilized for organic materials from process streams are generally not effective for the most volatile species in any case. Much of the sample loss is likely to be volatile hydrocarbons, which are separately determined by on-site chromatographic techniques.

It is usually desirable to add the prerequisite internal standards to the sample extract before volume reduction and liquid chromatography separation.(119) However, the analysis of a grossly complex mixture as envisioned here precludes addition of internal standards until qualitative analysis has been carried out, since it is impossible to prejudge the nature of the compounds present. High performance liquid chromatography separation techniques do however offer the significant advantage of truly quantitative sample fractionation. This largely obviates the usual necessity of adding internal standards before sample fractionation, since in the GPC and HPLC separations, the sample integrity is expected to remain above 90 percent.

Specific procedures have been recommended for both the Battelle Adsorbent Sampler train and the EPA SASS train; the former procedures are based upon 2 years of experience in the field, together with two laboratory validation studies for EPRI (113,119).

Battelle Adsorbent Sampler Train--

Specific sample extraction procedures for this sampling train include ultrasonic extraction of the quartz fiber filter with methylene chloride, and continuous extraction of the Tenax adsorbent trap with pentane followed by methyl alcohol.

Sample extraction from the Adsorbent Sampler is achieved by means of Soxhlet extraction with pentane followed by methyl alcohol. 100 ml of each solvent is required to achieve extraction of an Adsorbent Sampler. The sampling probes and hot filters from the sampling system were subjected to methylene chloride extraction. Internal standards are added to the combined extracts from each sampling train prior to volume reduction to approximately 1 ml by rotary evaporation and Kuderna-Danish evaporation.

EPA SASS Train--

A protocol for recovery of organic material from the SASS train has been developed by EPA (113). A schematic diagram for recovery from each component of the train is shown in Figures 9 and 10.

Validation of Stack Sampling Systems for Organic Material

Any stack sampling system used for measurement of hazardous organic materials must initially be evaluated with regard to collection of materials of concern. There are many variables associated with sampling of stack gases which may influence the performance of a sampling system including:

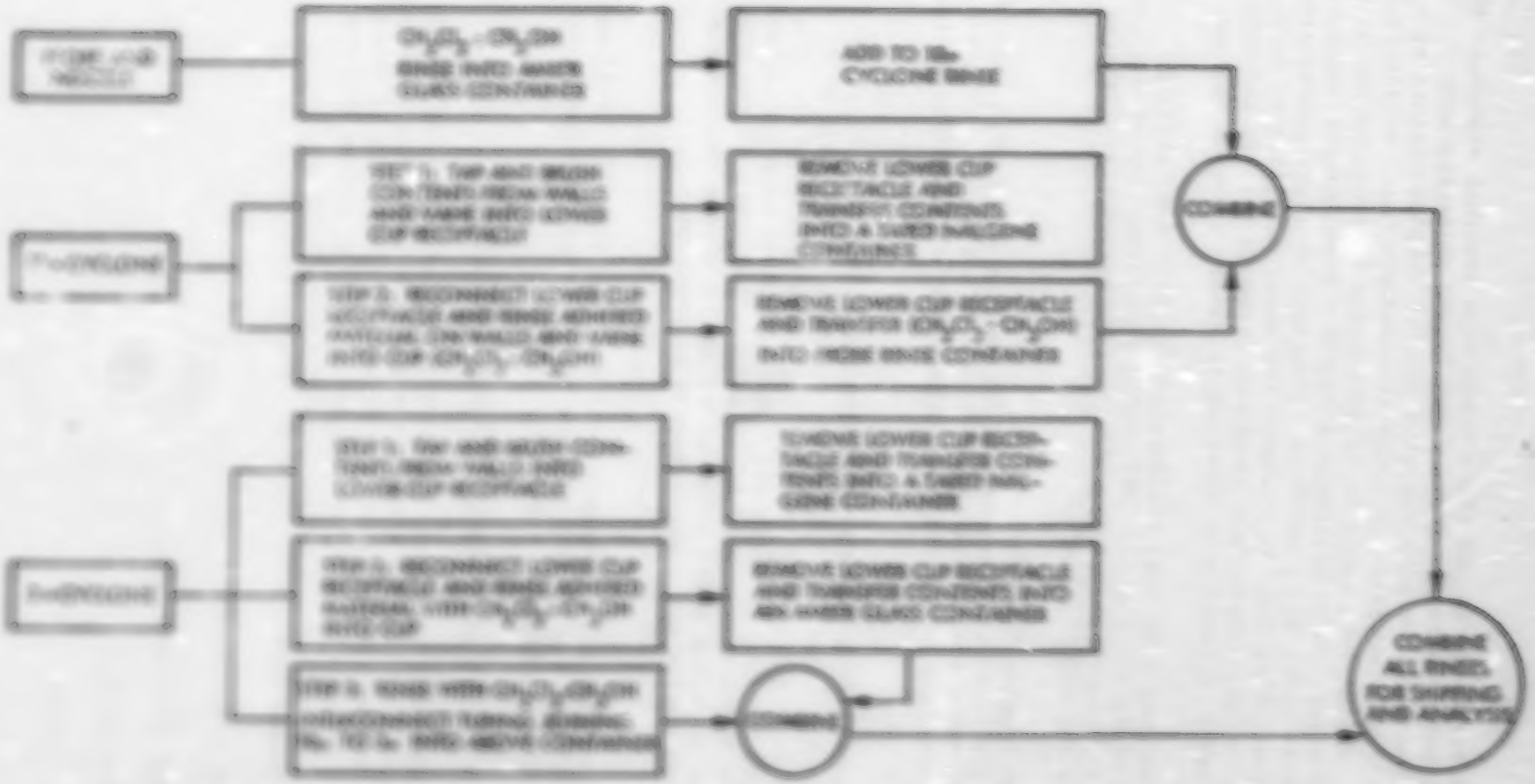
Stack temperature

Sampler temperature

Sampling flow rate

Nitrogen oxides

Sulfur oxides


COMBINE
COMBINE
COMBINE
ALL RINSES
FOR SHIPPING
AND ANALYSIS

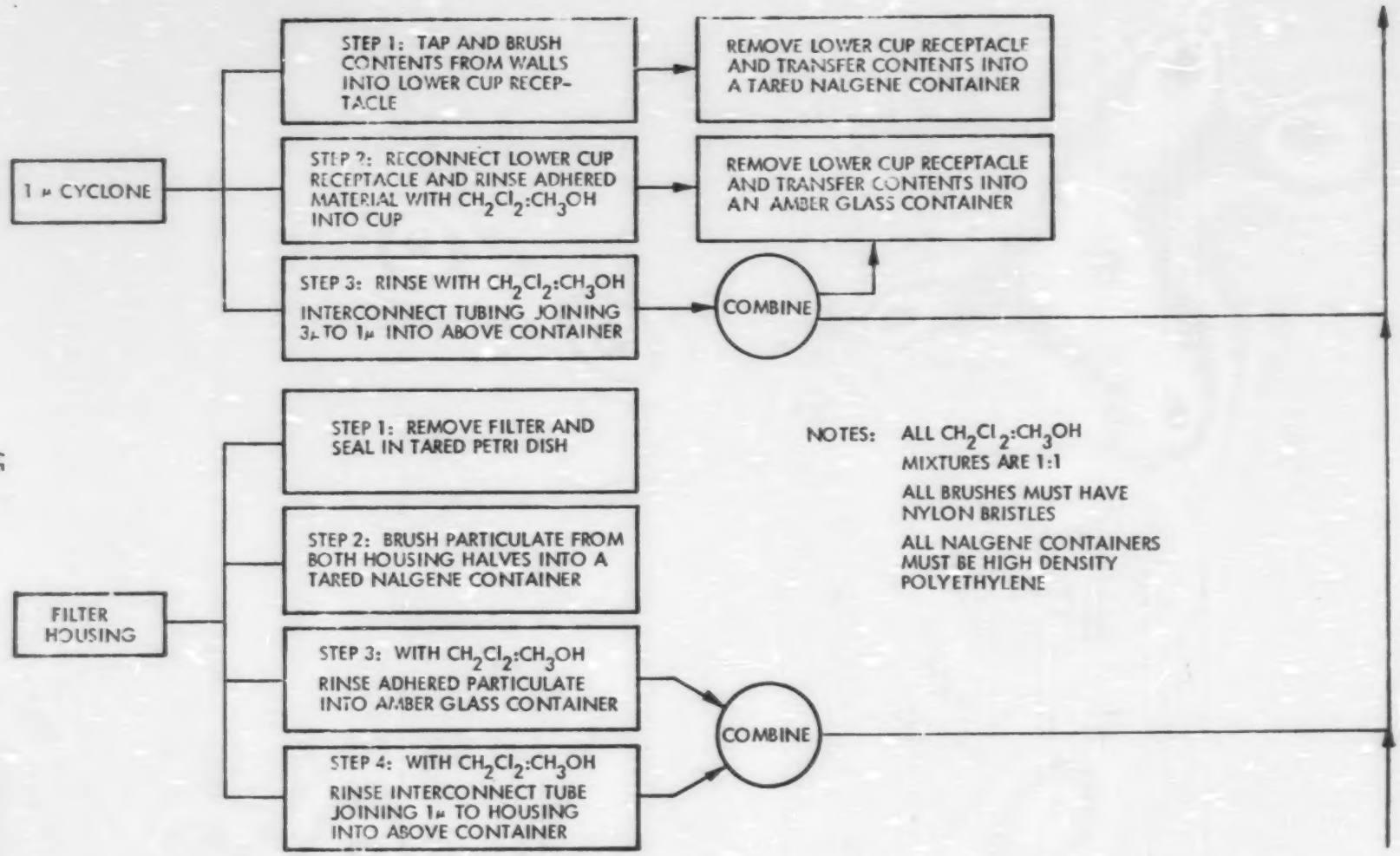

1 μ CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL WITH CH_2Cl_2:CH_3OH INTO CUP
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO AN AMBER GLASS CONTAINER
STEP 3: RINSE WITH CH_2Cl_2:CH_3OH INTERCONNECT TUBING JOINING 3μ TO 1μ INTO ABOVE CONTAINER
COMBINE
FILTER HOUSING
STEP 1: REMOVE FILTER AND SEAL IN TARED PETRI DISH
STEP 2: BRUSH PARTICULATE FROM BOTH HOUSING HALVES INTO A TARED NALGENE CONTAINER
STEP 3: WITH CH_2Cl_2:CH_3OH RINSE ADHERED PARTICULATE INTO AMBER GLASS CONTAINER
STEP 4: WITH CH_2Cl_2:CH_3OH RINSE INTERCONNECT TUBE JOINING 1μ TO HOUSING INTO ABOVE CONTAINER
COMBINE
NOTES: ALL CH_2Cl_2:CH_3OH MIXTURES ARE 1:1
ALL BRUSHES MUST HAVE NYLON BRISTLES
ALL NALGENE CONTAINERS MUST BE HIGH DENSITY POLYETHYLENE

FIGURE 9. (Continued)

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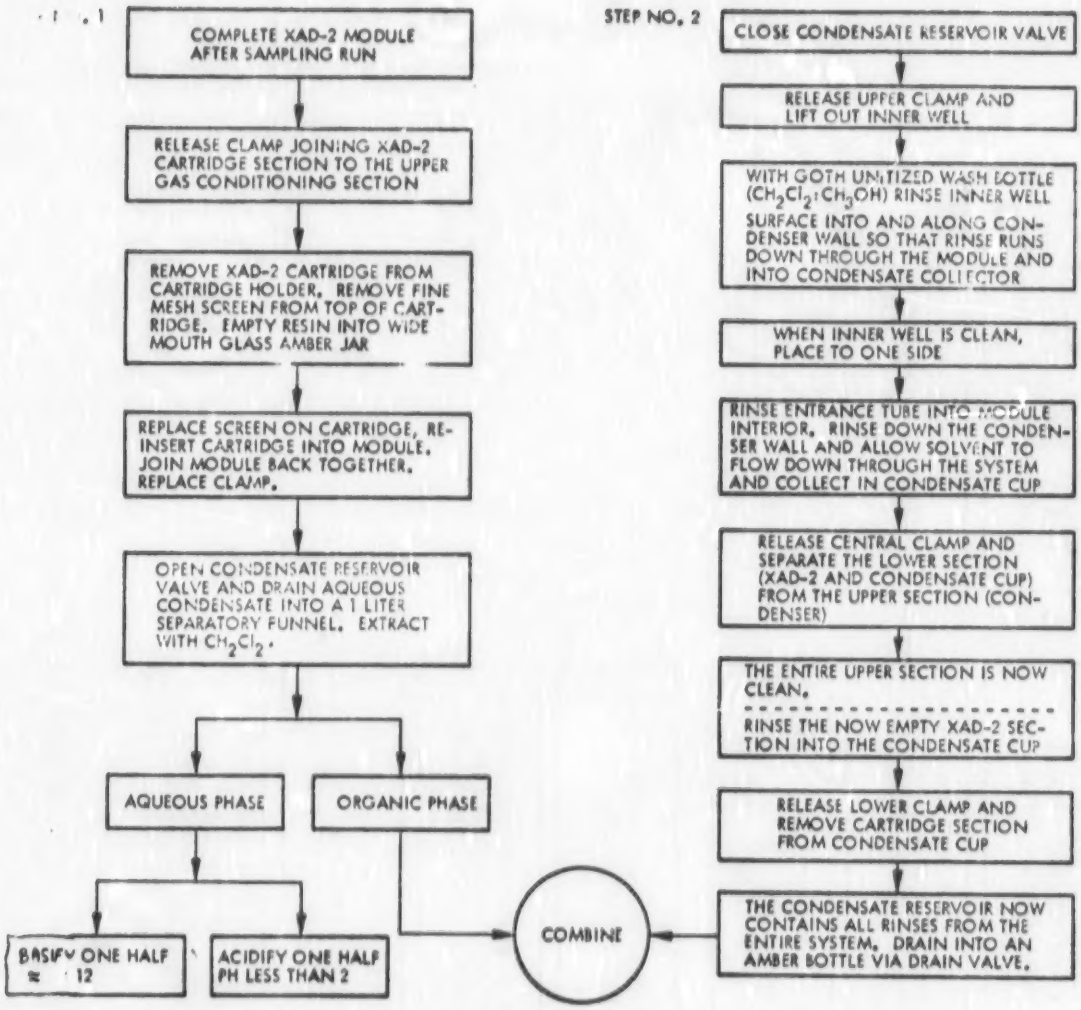
STEP NO. 1
COMPLETE XAD-2 MODULE AFTER SAMPLING RUN
RELEASE CLAMP JOINING XAD-2 CARTRIDGE SECTION TO THE UPPER GAS CONDITIONING SECTION
REMOVE XAD-2 CARTRIDGE FROM CARTRIDGE HOLDER. REMOVE FINE MESH SCREEN FROM TOP OF CARTRIDGE. EMPTY RESIN INTO WIDE MOUTH GLASS AMBER JAR
REPLACE SCREEN ON CARTRIDGE, REINSERT CARTRIDGE INTO MODULE. JOIN MODULE BACK TOGETHER. REPLACE CLAMP.
OPEN CONDENSATE RESERVOIR VALVE AND DRAIN AQUEOUS CONDENSATE INTO A 1 LITER SEPARATORY FUNNEL. EXTRACT WITH CH_2Cl_2.
AQUEOUS PHASE
ORGANIC PHASE
BASIFY ONE HALF ≈ 12
ACIDIFY ONE HALF PH LESS THAN 2
COMBINE
STEP NO. 2
CLOSE CONDENSATE RESERVOIR VALVE
RELEASE UPPER CLAMP AND LIFT OUT INNER WELL
WITH GOTH UNITIZED WASH BOTTLE (CH_2Cl_2:CH_3OH) RINSE INNER WELL SURFACE INTO AND ALONG CONDENSER WALL SO THAT RINSE RUNS DOWN THROUGH THE MODULE AND INTO CONDENSATE COLLECTOR
WHEN INNER WELL IS CLEAN, PLACE TO ONE SIDE
RINSE ENTRANCE TUBE INTO MODULE INTERIOR. RINSE DOWN THE CONDENSER WALL AND ALLOW SOLVENT TO FLOW DOWN THROUGH THE SYSTEM AND COLLECT IN CONDENSATE CUP
RELEASE CENTRAL CLAMP AND SEPARATE THE LOWER SECTION (XAD-2 AND CONDENSATE CUP) FROM THE UPPER SECTION (CONDENSER)
THE ENTIRE UPPER SECTION IS NOW CLEAN.
RINSE THE NOW EMPTY XAD-2 SECTION INTO THE CONDENSATE CUP
RELEASE LOWER CLAMP AND REMOVE CARTRIDGE SECTION FROM CONDENSATE CUP
THE CONDENSATE RESERVOIR NOW CONTAINS ALL RINSES FROM THE ENTIRE SYSTEM. DRAIN INTO AN AMBER BOTTLE VIA DRAIN VALVE.

FIGURE 10. SAMPLE HANDLING AND TRANSFER - XAD-2 MODULE

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Water vapor

Loading of organic materials.

Unless the impact of each of these variables has been evaluated prior to the utilization of a sampling system in this field, the value of the data subsequently obtained are of doubtful value.

To date, the only reported data for comprehensive validation of a stack sampling system have been obtained by Battelle's Columbus Laboratories for the Battelle Adsorbent Sampler, under laboratory simulated stack conditions (113). In this study, pre-purified air was heated to 400 F, precisely known quantities of nitric oxide, sulfur dioxide, water vapor, and up to 13 organic compounds were added, and the resultant gases were passed through a Battelle Adsorbent Sampler. Sample recovery and analysis was accomplished as described earlier. The specific variables used on this study were chosen to reflect extremes normally encountered under actual stack sampling, in order to realistically challenge the sampling system under precisely measurable conditions. The variables chosen were:

Sulfur dioxide:	200 and 2000 ppm
Nitric oxide:	150, 500, and 1500 ppm
Water vapor:	2, 4, and 8 percent by volume
Sampler temperature:	80, 105, 130, 155, and 180 F
Organic compound level:	10 and 50 μg each.

In order to elucidate the effects, if any, of both individual variables and combinations of variables, two fractional factorial statistical experimental designs were selected. The actual organic materials investigated on the study were selected on the basis of their being representative of hazardous organic materials which may be encountered on actual field situations; the materials subject were:

γ-butyrolactone

bis-2-chloroethylether

N-nitrosodiethylamine

Methyl methanesulfonate

Styrene oxide

p-Cresol

Benzoic acid

Terephthalic acid

1,2,3,4-Tetrachloronahpthalene

2,2',5,5'-Tetrachlorobiphenyl

Pyrene

Chrysene.

The comprehensive matrix of data obtained for these organic materials as the sampling parameters were varied and are described subsequently.

Preliminary experiments indicated that the selected organic could be divided into two groups on the basis of volatility. The more volatile materials, the first six in the above list, were subsequently validated over the 80-130 F temperature range in the Mark II Adsorbent Samplers. The less volatile group, the latter six compounds in the above list, were validated in the Mark I Adsorbent Sampler over the 130-180 F temperature range.

Of the variables studied in the less volatile group only the organic compound level had a statistically significant effect on the recovery, and only on two of the compounds studied. Recoveries averaged 79 percent at a level of 50 μg, and 72 percent at a level of 10 μg. For the more volatile compound group, relative humidity, sampler temperature, and organic compound level were studied. Overall, sampler temperature and organic compound level were statistically significant variables; percentage recoveries were highest at the lowest temperatures (80 F) and highest organic compound level (50 μg). However, there were variations in effects between the different compounds. Recoveries were lowest for compounds with the lowest boiling point due to losses during the concentration step just prior to analysis.

The statistical analysis revealed that of the variables studied in the less volatile compound group, only compound loading level had a statistically significant effect on recovery of any of the organic compounds. Even the loading level had no statistical effect for chrysens, TCN, and TCB. For terephthalic acid, recoveries were so low that valid statistical inferences cannot be drawn. Average recoveries for the various compounds are listed in Table 2.

For the more volatile components group, statistical evaluation by the technique of analysis of variance provides the following conclusions. No methyl methanesulfonate and γ-butyroloctane were recovered in the experiments and hence, were excluded from the table and the statistical analysis.

(1) For the total set of data (i.e., all four compounds) only sampler temperature and compound loading had a statistically significant effect on recoveries.

(2) For styrene oxide none of the variables had a statistically significant effect on recoveries. The average recovery was 42 percent.

TABLE 2. RECOVERIES IN STACK SAMPLER VALIDATION STUDY

Compound	Percent Recovery at Loading	
	50 µg	10 µg
Benzoic acid	72	54
Terephthalic[a]	1(2)	6(14)
Pyrene	80	67
Chrysene[b]	68	73
TCN[b]	77	69
TCB[b]	96	97

(a) The recoveries of terephthalic acid were so low that valid inferences could not be drawn. Recovery was zero in half of the experiments. The value in parenthesis is the average of those experiments if recovery was not zero.

(b) The differences in recovery between the two loading levels is not statistically significant.

(3) For p-cresol, sampler temperature, relative humidity, and interaction (combined effect) of compound level and relative humidity had a statistically significant effect on recoveries. The average recovery of all experiments was 74 percent. Recoveries were highest at 25 C (108 percent average), and 50 percent relative humidity (95 percent average). The combination of 50 percent relative humidity and 50 µg loading give the highest recoveries (102 percent average).

(4) For N-nitrosodiethylamine only relative humidity has a statistically significant effect on recoveries. The average recovery of all experiments was 22 percent. The highest recoveries were obtained at 50 percent relative humidity (35 percent). Although the effect of temperature was not statistically significant the recovery at sampler temperature, 25 C, (30 percent) was higher than at the higher temperatures.

(5) For chloroethyl ether only compound loading and temperature had a statistically significant effect on recoveries. The average recovery was 45 percent. The highest recoveries were obtained at the 50 µg loading level (62 percent) and at a sampler temperature of 25 C (67 percent).

The results are summarized in Table 3 in which recoveries are listed. The average for and the level of each variable at which the highest recoveries were obtained are listed. Those variables which are statistically significant are indicated by an asterisk.

TABLE 3. MAXIMUM RECOVERIES FOR SAMPLER VALIDATION WITH MORE VOLATILE COMPOUNDS[a]

	At Temperature	At Loading	At Percent RH
Styrene oxide	59 (55 C)	45 (50 µg)	43 (50)
p-Cresol	106* (25 C)	79 (50 µg)	95* (50)
N-Nitrosodiethylamine	30 (25 C)	25 (50 µg)	35* (50)
Chloroethyl ether	67* (25 C)	62* (50 µg)	54 (10)

[a] Asterisked values are for statistically significant variables.

Some of the low recovery results obtained in these two statistical studies were surprising, since for both groups no sampler breakthrough exceeding approximately 15 percent of the highest organic compound loading was ever observed in the preliminary studies. This finding strongly suggests that sample losses are exaggerated in the recovery and handling of samples from the Adsorbent Sampler. It would appear that there is an urgent need for research pertaining to the efficient recovery and concentration of solvent extracts from such sampling devices.

The selection of sorbent for the adsorbent sampling module must also be considered; polymeric adsorbents used for this purpose should have the following characteristics:

(1) High surface area to permit adsorption of large amounts of ambient pollutants.

(2) Satisfactory particle size to minimize pressure drop across adsorbent bed.

(3) High column efficiency to permit adsorption of contaminants from a large volume of air.

(4) High specificity for adsorption of the contaminants of interest, and a low degree of adsorption of water vapor and hydrocarbons which are often present at high levels relative to other contaminants.

(5) Compatibility with solvents used for sample recovery.

Recent work by Butler and Burke (122), has characterized various porous polymers as adsorbents in sampling devices in terms of their surface areas and adsorption efficiencies.

The two adsorbents which are most commonly used in stack sampling applications are Tenax GC and XAD-2. While most experience has been gained to date with Tenax GC, there is reason to believe that XAD-2 may ultimately prove to be the adsorbent of choice. Besides cost considerations, which favor XAD-2, XAD-2 has greater surface area and thus has a potentially higher adsorbent capacity (122). The physical characteristics of Tenax and XAD-2 favor XAD-2, since higher flow rates may be attained through XAD-2 than on equal volume of Tenax. Finally, Tenax has been shown to be readily depolymerized under certain stack gas sampling conditions (119,123), and has been demonstrated to have a significantly higher solvent extraction blank than XAD-2 (124). Such background contamination may be relatively unimportant when carrying out analyses for specific compounds, when the blank is often eliminated by LC or HPLC cleanup procedures. However, for survey analyses such as Level-1 (90,115), adsorbent background contamination may create serious problems, and for this reason Battelle-Columbus Laboratories have discontinued the use of Tenax in favor of XAD-2 when multi-specie analysis are to be carried out.

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